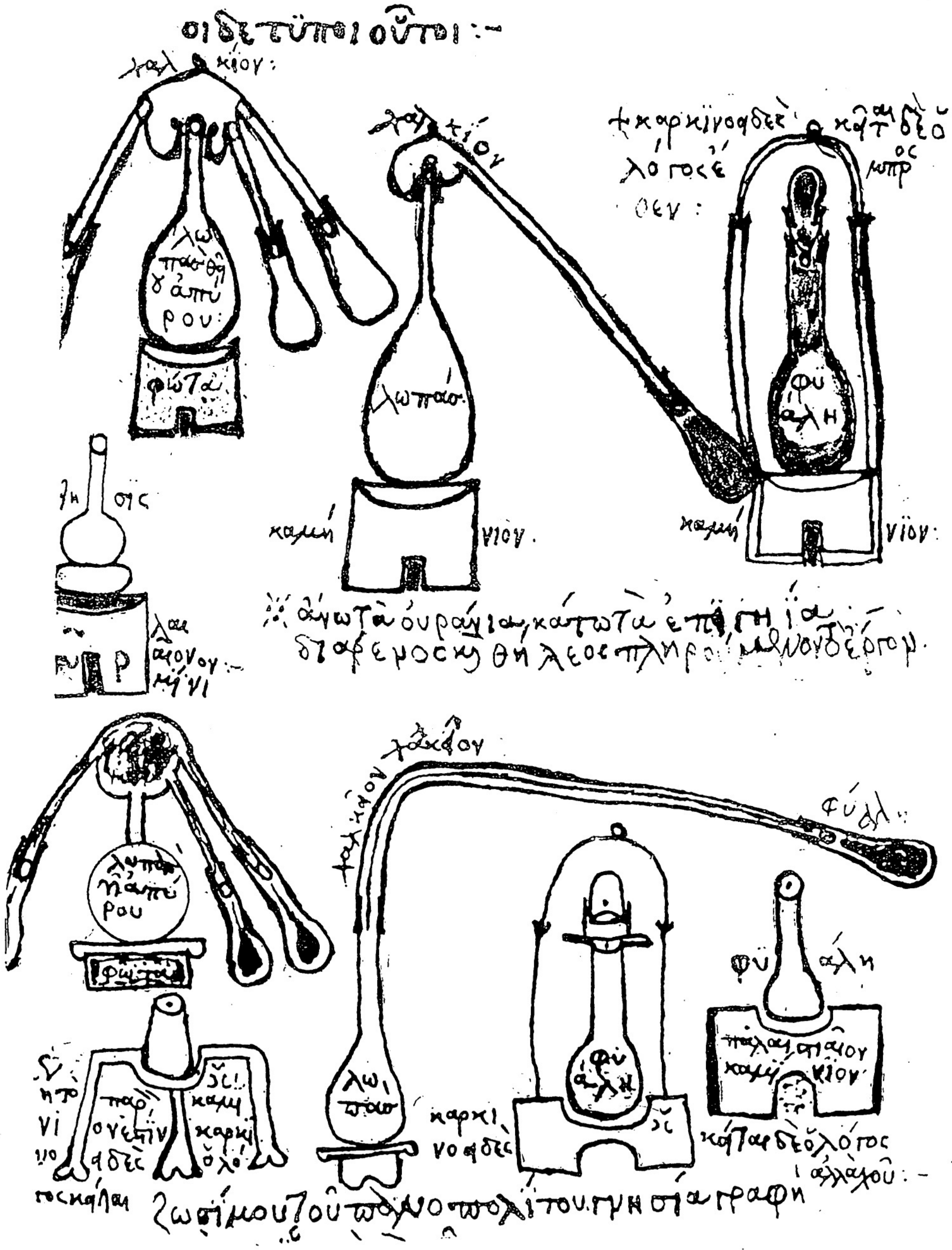
BULLETIN FOR THE HISTORY OF CHEMISTRY

Division of the History of Chemistry of the American Chemical Society

VOLUME 47 Number2 2022



Distillation Technology

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The Cover... Distillation apparatus depicted in Hellenistic manuscripts (p 179)

LETTERS TO THE EDITOR

St. Elmo Brady

To the Editors:

As a follow-up to our recent article in the *Bulletin* on the American chemist St. Elmo Brady ("St. Elmo Brady (1884-1966): The First African American Chemistry Doctorate Recipient," *Bull. Hist. Chem.*, **2021**, *46*(1), 83-107), I would like to alert your readers to the acquisition by the Science History Institute of a previously unknown book by Brady, *Elements of Metallurgy for Dental Students*, which was published in 1923 or 1924. The Science History Institute has posted digital images of the entire book (see https://digital.sciencehistory.org/works/37uhevn). As far as we know, this holding is unique—no other copy of this book seems to be recorded; SHI obtained their copy by purchase through Ebay. We have added an updated list of all of St. Elmo Brady's publications, including this latest addition, to the Supplementary material available for our article.

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HIST Centennial Issue

To the Editors:

Kudos to Carmen J. Giunta and Jeffrey I. Seeman for their outstanding effort as editors of the HIST Centennial Issue of the *Bulletin (Bull. Hist. Chem.,* **2022***, 47*(1)*)*. In addition to their own excellent contributions, they assembled a diverse, world-class team of authors to tackle a complex and multifaceted subject.

Since my retirement I pursued research that is best described as being at the intersection of the History of Chemistry and the History of Art, with emphasis on the chemical history of artists' recipes. The essays in the Centennial Issue have caused me to rethink, and critically reflect on my own work in many ways. While space and time do not permit me to comment on all of them, I would like to address several that are near and dear to my heart.

Mary Virginia Orna's essay aptly points out the increasing role of Archaeological Chemistry (AC) in art conservation. The current trend in conservation science is to use materials that are authentic both in their composition and manner of preparation and avoid anachronisms. Clearly AC, aided whenever available by historical and archival recipes, would play a key role in guiding such efforts. As Orna points out, replication experiments are important in enhancing our understanding of the processes and practices even when recipes are available, since most recipes prior to the 19th century can be quite ambiguous. The significance of replicates is also echoed in Alan J. Rocke's essay, when he mentions the work of Columbia University historian Pamela H. Smith. The development of laboratory instruments, often mentioned in recipes is, as Rocke suggests, another open field for new studies in the history of chemistry.

The inescapable nexus between the concepts of "*the recipe*" and "*the experiment*" brings to the fore the latent tension between the chemist-historian and the historian/philosopher of science. Borrowing from ceramic history, I have always maintained for example, that the attempts of alchemists in Late Medieval-Renaissance Europe, and more significantly of Islamic alchemists before them, to make Chinese hard-paste porcelain were guided by the peripatetic doctrine of matter and form. Their efforts led to imitations of Chinese porcelain that could be commercialized as such (fritware, tin-glazed earthenware Medici porcelain etc.) but the original intent was to reinvent rather than imitate, and I think philosophical doctrines played a role in that effort. Discussing the experiments of Ehrenfried Walther von Tschirnhaus with ceramic materials is even more challenging, for one needs to first understand his epistemological approach to the notion of "*experiment*" itself. Tschirnhaus was heavily influenced by Descartes, was a close associate of Spinoza, and had also spent time with Robert Boyle, three towering figures who held very different views on the nature and usefulness of "*experiment.*" In such instances, it is essential that the chemist-historian closely collaborates with the historian of chemistry whose formal academic training includes a background in the history of philosophy. The opportunities and challenges inherent in such collaborations are discussed very lucidly by Peter J. T. Morris and Seeman.

Finally, Giunta's essay on Presentism forces us to re-examine our own methodological approach to our research. Presentism does have some salutary aspects. Interpreting ancient experiments using the chemical knowledge and analytical tools of today helps us understand why artisans, alchemists and early chemists succeeded or failed in their endeavors and the role of insight vs happenstance in determining the outcome.

In short, this is a remarkable Special Issue that deserves a special place on the bookshelf of everyone seriously interested in the subject.

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MOTHER OF INVENTION: MARIA THE JEWESS AND EARLY CONTRIBUTIONS TO CHEMICAL APPARATUS

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Introduction

Current practitioners rarely acknowledge the influence of early alchemical practices on modern laboratory activities. While chemical practice can be traced deep into antiquity with a variety of chemical technologies (pigments, ceramics, metals, glass, etc.) (1), it is in alchemy that one can see the beginnings of our ongoing efforts to understand matter and its trans-formation (2). Of course, views of alchemy are hindered by associations with magic and the occult, but its practice also included the practical study of minerals, metals, and the making of medicines (2, 3). In particular, it is not possible to read the works of early alchemists such as Pseudo-Democritus or Maria the Jewess without feeling that these are practical metallurgical efforts undertaken with a specific purpose, even though mystical and religious elements are present (4). In the process, alchemists also introduced a number of innovations and inventions in terms of apparatus and equipment, many of which are still in use in the modern chemical laboratory (2. 3, 5). At the same time, it may be noted that a number of female practitioners can be found during the early alchemical period, including Maria the Jewess, the alchemist Cleopatra, Paphnutia the Virgin, and Theosebeia, the sister of Zosimos (6). Of these, Maria the Jewess is a particularly important, if enigmatic, figure. An alchemist of the first century CE during the Greco-Egyptian period, she wrote on practical aspects of the chemical arts and described various types of early laboratory apparatus (2, 4,7-12). As such, the following aims to review what is known about Maria, while highlighting some of her most important contributions to chemical apparatus.

Figure 1. *Engraving depicting Maria the Prophetess from Michael Maier's* Symbola Aurea Mensae Duodecim Nationum*, 1617.*

Maria the Jewess

Unfortunately, knowledge of Maria and her life is extremely limited, and is mainly restricted to writings ascribed to her, which survive largely only as quotations by the later alchemist Zosimos of Panopolis (ca. 300 CE) (4, 6, 8, 11-15). Still, this has not stopped artists from

envisioning what she may have looked like, as illustrated with the depiction of her by the German alchemist Michael Maier (1568-1622) shown in Figure 1. In his writings, Zosimos referred to her in Greek as simply *Μαρίᾳ* (16), which can be translated as either Mary or Maria. As such, it is common to see both names used throughout various accounts, although some have also given her name as Miriam (4, 6, 7, 9, 11, 13, 14, 17).

Over time, authors began referring to her in Latin as *Maria Hebraea,* in order to better specify exactly who was being discussed. While this can be translated literally as Maria the Hebrew, the name Maria the Jewess is by far the most commonly used throughout the alchemical and chemical literature. It should be pointed out that, in modern context, the term "Jewess" can sometimes be viewed as dated or offensive (18), but this was not the case in its original early use. The modern negative view of the word is believed to be the result of its use as a slur by various anti-Semitic groups and has been traced to the later 20th century (19), with the word included in dictionaries published as late as the early 1980s without any reference to such negative connotations (20). Even still, at least some in the modern Jewish community wish to reclaim the word and return it to its original proud use (19).

In addition to Maria the Jewess, some alchemical texts described her as Maria the Prophetess (*Maria Prophetissa*) beginning in the early 16th century, while later Arabic sources also used the name Maria the Copt (*Mariya al-Qibtiyya*) (12, 21). Still, the frequency of these alternate names is small in comparison. Her Jewish heritage seems to be confirmed in one of the fragments of her writings, which refers to her being of "the race of Abraham" (4, 7, 9, 12, 15). In addition, she is alleged by some to be the sister of Moses (4, 11, 12, 15, 21, 22). At the same time, she has also been associated with the Gnostic sects (21) and her name has been included in lists of ecumenical alchemists (22).

Still, although little is really known about her beyond quoted writings, Maria is a critical figure in the history of chemistry. She has been repeatedly praised as one of the earliest and most important alchemists and is listed as such in the *Kitāb al-Fihrist* of Ibn al-Nadim (d. 995 or 998 CE), a 10th century compendium of Islamic knowledge (12, 15, 23, 24). In particular, the works quoted by Zosimos tell us that a great number of practical instruments were devised by her, including distillation apparatus, the kerotakis apparatus, as well as various types of heating baths and furnaces (2, 4, 6, 8, 10-12, 14, 15, 17, 22, 25). She also discussed the importance of glass bottles as they allow "seeing without touching" and the safe handling of harmful substances such as mercury (12, 15).

Balneum Mariae (Bain-marie)

Of these various inventions, the one most commonly associated with Maria is the *balneum Mariae* (bath of Maria), more commonly known now as the *bain-marie*, a modification of the older French name *bain Marie* (2, 4, 7, 11, 12, 14, 17, 22, 25). The original term balneum Mariae is thought to have been first introduced by Arnald of Villanova (c. 1240-1311) in the 14th century (11). In later German manuscripts, it is known as the *Marienbad* (12, 23) and by the 17th century was sometimes referred to with the simple abbreviation *B.M.* (26).

The balneum Mariae is most commonly described as a water-bath used in chemical processes where gentle heat is necessary (4, 16, 23, 27), which is certainly consistent with the modern bain-marie commonly applied in culinary practice, sometimes also referred to as a double boiler. However, if the original balneum Mariae was just a simple water-bath, it is unclear why it bears Maria's name or why she is credited with its invention, as references to simple water-baths can be found in the writings of several previous authors (23, 25). As outlined by the German chemist and historian Edmund von Lippmann (1857-1940) (23), such references can be found as early as the 5th century BCE in the writings of the Greek physician Hippocrates of Kos (c. 460-c. 370 BCE). Later, the Greek philosopher Theophrastus (c. 371-c. 287 BCE) also described the application of a water-bath for the extraction of perfumes from flowers and spices with oils (23, 28):

> But in all cases the cooking, whether to produce the astringent quality or to impart the proper odour, is done in vessels standing in water and not in actual contact with the fire; the reason being that the heating must be gentle, and there would be considerable waste if these were in actual contact with the flames; and further the perfume would smell of burning.

Additional references can also be found in the writings of the Greek physician Dioscurides (c. 40-90 CE) and the Roman author Pliny the Elder (c. 23-79 CE) (23).

Based on these previous reports, one of three possible conclusions can be made. Either the origin of the water bath is incorrectly attributed to Maria, or perhaps she popularized its use in chemical applications, even if it was not her original innovation. The third possibility is that the term balneum Mariae originally referred to a particular apparatus used to apply heated water to vessels.

Of these, von Lippmann argued that the balneum Mariae owes its name to the interconnection of a number of very remote circumstances that are only indirectly related to Maria the Jewess and not due to her introduction of the device (15, 23).

However, arguments can also be made for the third case. In the 1612 edition of *A Lexicon of Alchemy*, written by the German alchemist Martinus Rulandus (1532-1602), three separate entries are given for balneum Mariae. The definitions given include 1) warm water; 2) the dissolution of a substance in a suitable vessel of warm water; 3) a distillatory furnace containing water, into which a chemical vessel is placed (29). None of these refers directly to a general water bath, with the third seemingly referring to a particular apparatus that combines a furnace with a water bath. Other authors have also referred to the balneum Mariae as a double-walled heating vessel filled with water, again inferring a specific device, that has survived into the present as the indispensable water bath (14). Thus, it is possible that over time the use of the term balneum Mariae evolved from the name of a particular device (such as a combined furnace/water bath) to an overall reference to the water bath in general. If so, this would not be the first time that the meaning of a chemical term has changed over time (30, 31).

Distillation Apparatus

A particularly important apparatus in the practice of the chemical arts, that was first described by Maria, is the still (6, 8, 12, 15, 32, 33). Although it is not known if the basic three-part still was truly her innovation (13) she is generally given credit for its invention (6, 8, 16, 25, 33). In her writings quoted by Zosimos, the development of the apparatus is already fairly advanced, with the specific still described being a three-armed variant known as a *tribikos* (8, 10-13, 15, 22, 25, 33). As quoted by Zosimos (34):

> Then I will outline the tribikos for you. This is what we call the (directives) which is made from (copper) without shadow, (and) therefore the technical details have been transmitted by Mary. It looks like this: Make, she said, three rolled copper pipes—that the sheet is thin, having the thickness (of) a strainer, or a little thicker, like (the) copper of a galette pan—a cubit and a half long. So, make three pipes of this type. Also make a large cauldron, about the size of a cubit minus a palm; with the opening of the cauldron proportionate. Let the three pipes have an opening similar to (that of the) neck of a light bikos. The (pipe-) thumb being (…?), (It is necessary) that there are two (pipes-) fingers adapted to the sides of the cauldron on both sides, towards the bottom; and in this bottom, three holes adapting to the pipes; once adjusted, (let these) be welded extraordinarily well, because that which comes from above contains vapor. And after having placed the cauldron over a terracotta cucurbit containing sulfur, after having wrought all around the joints with flour paste, put, at the ends of the pipes, large, thick bikos of glass, so that they do not break under the effect of the heat of the water, heat that conveys what rises.

Representative illustrations of distillation apparatus from Hellenistic manuscripts of this time period are given in Figure 2. It must be highlighted that these figures come from copies of these manuscripts dating centuries after that of the originals. As such, it is unknown how many times these figures were recopied, nor what errors, distortions, or modifications may have been introduced in the process (6, 8, 33). However, they do seem to correspond to the descriptions given in the associated texts.

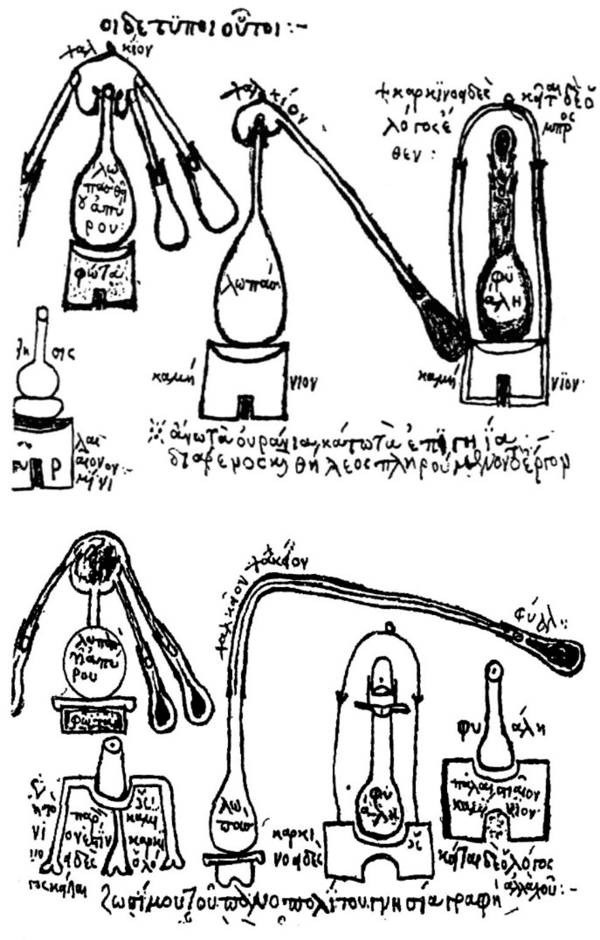

Figure 2. *Depictions of early chemical apparatus from Hellenistic manuscripts (M. Berthelot,* Introduction à l'étude de la Chimie des Anciens et du Moyen Age*, Steinheil, Paris, 1889).*

In contrast to the tribikos, the simplest form of the still utilizes only a single receiver, examples of which can be seen in Figure 2. The early traditional still consisted of three components (Figure 3): the distillation vessel (*cucurbit*), the still-head (*άμβιξ, ambix*, or *φιάλη, phiale*; Figure 4) with an attached delivery tube (*σωλήν, sōlēn*), and the receiving vessel *(βίκος, bikos*) (15, 16, 25, 32, 33). The name cucurbit comes from the Latin *cucurbita* meaning gourd (25). The cucurbit was originally called bikos as well, along with the alternate terms *lebes*, *lopas*, and *botarion* (15, 25, 32, 33). Although most sources use the term ambix to refer to the still-head, more recent scholarship has revealed that alternate terms such as phiale were more commonly used in this way, with ambix usually used to refer to the still as a whole (32). Prior to this, the use of ambix for the complete still has generally been viewed to be a later practice (8, 16, 22, 25, 33). The bikos receiving vessels were generally comprised of a small body with a long thin neck and such flasks in general were also called a *phial* (15, 25, 32). As such, these can be viewed as the early ancestor of the modern round-bottom flask.

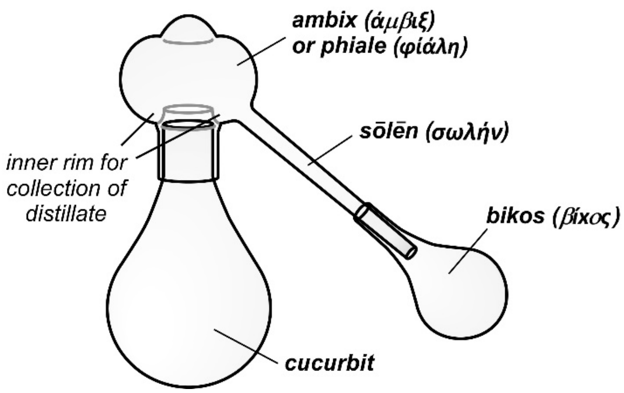

Figure 3. *Basic components of the early still (Ref. 31; adapted with permission from Springer Nature).*

The name tribikos given in the quote of Maria refers to the fact that this form of still utilized three receiving vessels, with both tribikos and dibikos apparatus known. It is unclear whether these types of stills were meant to be used for two or more fractions or for the simultaneous collection of distilled material in multiple receivers (32). In terms of practical application, simultaneous collection would be the simplest possible use.

These early stills were made from a mixture of primarily earthenware (often with the interior glazed, Figure 4), copper, and glass (8, 17, 32, 33, 35). During this early period, however, glass was generally limited to just the receiving vessels (32, 33), which were not subjected to heating and where transparency was a critical factor (36). The individual pieces of the still were fixed together using a lute, which was a material to seal the joints between the components, particularly between the curcurbit and the still-head. The lute needed to exhibit adequate plasticity and a variety of materials have been reported to be used for this purpose. As quoted by Maria, an early lute was a flour paste, but other reported materials have also included fat, wax, clay, lime mixed with egg white, and an oil mixture of gypsum or clay (17, 22, 25, 33, 35).

Figure 4. *Modern replica of an earthenware still-head without the solen, which has been halved to show the interior detail. (Islington Education Library Service).*

During the 7th-8th centuries CE, the term ambix was transformed via Islamic philosophers through the addition of the Arabic article *al-* to become *al-anbîq*, which eventually became *alembicus* and *alembic* (17, 22, 25, 32, 33, 35), the latter of which is the most common name for the still in the later periods. Due of the Arabic origin of the word alembic, some authors have mistakenly attributed the discovery of distillation methods to later Islamic philosophers (32).

Kerotakis

Another apparatus for which Maria is credited is called the kerotakis, which is a reflux apparatus designed for treating metals with vapors (4, 11-14, 17). Figuring prominently in Greek alchemical writings, it is believed that it finds both its name and origin in the artist's palette (6, 11-13, 17, 22, 25, 32). It is generally viewed that kerotakis originally referred to an artist's palette that consisted of a metallic plate, often triangular in shape with rounded ends, that has been compared to a modern bricklayer's trowel (6, 11, 12, 22, 37). Greek and Roman artists of the time practiced an encaustic painting technique, which involved painting with a mixture of pigment and melted wax. As a consequence, their colors had to be kept hot during use by heating the palette over a small charcoal stove (7, 11-13, 17, 22, 32, 37). It has been proposed that the original intention was to soften

the metals in order to impregnate them with color in the same way that the wax of the artist was softened and mixed with pigment (12, 13).

In its application to alchemical operations, the palette was combined with additional components (13). The initial kerotakis was placed at the top of a cylindrical or spherical container, closed at the lower end, which contained a substance that would vaporize on heating (11, 13, 17, 22, 32). This container would then be placed on or within a furnace for heating the species to be vaporized (6, 32). A hemispherical condensing cover would then be luted into position over the palette (6, 11, 12, 17, 22, 37), with a small hole provided at the top to allow the escape of heated air. This hole could be again covered with a little inverted cup (13). This set of covers thus allowed the vaporized material to build up in concentration around the palette and/or to condense and flow back down into the base again (6, 13, 17, 32). A conjectural representation of this assembly was prepared by the British chemist and historian F. Sherwood Taylor (1897-1956), as shown in Figure 5 (4). While the term kerotakis initially referred to just the palette, it was later used to denote the apparatus as a whole (17).

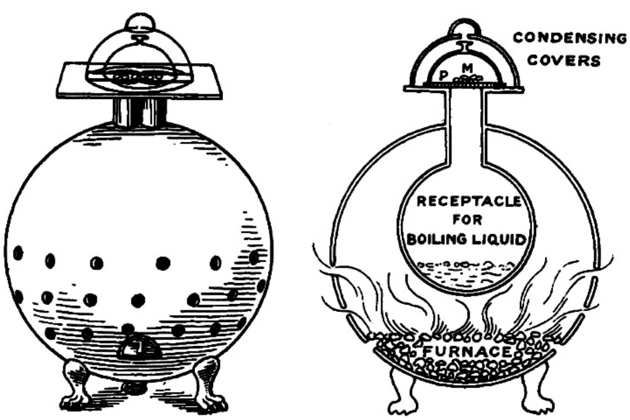

Figure 5. *F. Sherwood Taylor's conjectural representation of the spherical form of the kerotakis apparatus (Ref. 4, courtesy of JSTOR).*

During operation, the material to be vaporized would be added to the apparatus, typically sulfur, arsenic sulfides (orpiment, etc.), or mercury, and the metal to be treated would be placed on the palette, normally in the form of foil or powder (4, 6, 11, 13, 17, 22, 32). Metals treated in this way were most commonly copper or lead, but may have also included silver and gold (4, 6, 13). The fire was then started, causing vaporization and reaction with the metal sample on the palette. Excess vapor could also condense at the top of the apparatus and flow back to the bottom, maintaining a continuous reflux action (11, 13, 17). Later advances in design were in the direction of elaborating the heating and condensing arrangements, as well as introducing a form of grating or strainer to prevent fragments of metal species from being flushed off the palette and falling into the base (11, 13, 37).

Conclusions

As outlined in the above discussion, the contributions of alchemy to the introduction and evolution of chemical apparatus is a landmark moment in the history of chemistry. Furthermore, it is noteworthy that so much of this development is credited to a single practitioner, Maria the Jewess. Of course, considering the scarcity of documentation in this early period of alchemy, it is quite possible that others contributed to the innovations credited to Maria. Still, it is impossible to downplay the impact that these laboratory apparatus have had on the development and continued practice of the chemical sciences. As such, the practical contributions of alchemy to laboratory science cannot be understated, a relationship that every modern practitioner should be aware of. At the same time, it is unfortunate that the bulk of today's chemists do not recognize the name Maria the Jewess, someone whose contributions merit inclusion among more well-known figures such as Lavoisier, Dalton, or Berzelius.

Acknowledgements

I would like to thank the Department of Chemistry and Biochemistry of North Dakota State University (NDSU) for continued support of my historical research, and the NDSU Interlibrary Loan Department for its continued assistance in obtaining various elusive and obscure sources.

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Active in the fields of materials chemistry and the history of chemistry, his research interests include the design and synthesis of conjugated materials, photovoltaics, organic light emitting diodes, the history of materials, chemical technology in antiquity, and the application of history to chemical education. Prof. Rasmussen served as the Program Chair for the History of Chemistry (HIST) division of the American Chemical Society from 2008 to 2017 and currently serves as the division's Chair. In addition, he serves as the series editor for the book series *Springer Briefs in History of Chemistry* and *Perspectives on the History of Chemistry*, and as an advisory board member for the journal *Substantia: An International Journal of the History of Chemistry*.

HIST Presentations at ACS National Meeting Fall 2022

The following presentations are on HIST's program at the fall national meeting of the American Chemical Society set for Chicago on 20-25 August 2022. HIST's programming falls on 22 and 23 August.

General Papers

Carmen Giunta, Reform of weights and measures in late 18th-century France, Great Britain, and United States

Nicholas Zumbulyadis, Anticipating the turn of the 19th century: Cobalt chemistry recipes from the Meissen archives (1720-1730)

Nicolay Tsarevsky, Understanding the chemistry of the universe: Some early studies

Michael Renier, History and philosophy of computational chemistry

David Seigler, Guido Pauli and John Friesen, Vitamin P: Its perplexing history

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A COMMEMORATION OF ERNEST RUTHERFORD ON THE 150TH ANNIVERSARY OF HIS BIRTH PART II: 1907-1937

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Introduction to Part II

Part I of this article (1) traced the life and career of Ernest Rutherford (1871-1937) from his early life and education in New Zealand through his first stint at the Cavendish Laboratory in Cambridge and his tenure at McGill University in Canada. By this time he had already established himself as a Fellow of the Royal Society and one of the world's foremost researchers in radioactivity. We left Rutherford about to return to England to take up the chair of physics at Victoria University in Manchester.

When, in 1907, Rutherford arrived to take up his new professorship in Manchester, he chose to reside in a small suburb called Withington, about two miles distant from the university, necessitating a daily commute by tram car. He settled in well with the city and its people, whom he found welcoming and hospitable. However, it seems that his debut encounter with the faculty at Victoria University was anything but peaceful. The story goes that when he arrived in the physics department at Manchester, he discovered that "creeping appropriation" of space by the chemistry department had taken place during the interregnum. When he approached the podium at the first faculty meeting, he slammed his fist on it, roaring, "By thunder!" And after badgeringly following the head of chemistry back to his office, shouting not too complimentary imprecations, he had his space back within a couple of weeks (2). Lest this tale give the impression that Rutherford was implacably irascible, it is time to digress more fully on a description of his personality while we are midway in the story of his career.

Rutherford's Character and Personality

Rutherford has invariably been described by members of his family as fun-loving, interested in many things, kind to a fault in his relationships with his younger siblings, and very caring for his mother, as demonstrated by his bi-weekly letters to her describing almost every aspect of his life as he went along. The thrift and hard work that he learned from his family stayed with him throughout his life. His family's bedrock values became his characteristic traits: simplicity, directness, economy, and reverence for education (3). He was also described by his schoolmates in secondary school and at Canterbury College as very kind and eager to explain some of the finer points of physics. At the same time, we note his failure to appreciate the difficulties of his students as he frequently lectured over their heads or simply did not notice them if he were engrossed in an explanation.

In the Foreword to his biography by Arthur Stewart Eve (1862-1948), written by Earl Baldwin of Bewdley, former Chancellor of the University of Cambridge, he is described as "an unfailing source of inspiration which his collaborators and pupils found in him," displaying an "ever fresh and boyishly eager personality," with "patient kindliness" and "his almost uncanny gift for singling out from a mass of confusing detail the one significant fact."

Bewdley went on to remark on the boundless enthusiasm that radiated from him, that he was accessible and approachable to all his students, that he ranked them among his friends and was quick to praise and encourage. His criticism was always replaced by fresh and promising ideas to follow. And continuing (4):

> His shrewd insight and practical mind rarely if ever failed him nor was his aid ever invoked in vain … His refreshing personality, his dauntless spirit, ever-joyful enthusiasm: how can they be recaptured and confined within the limits of mere words!

Others have described him as "a force of nature," "charismatic," a "man of action." Yet another wrote (5):

> He was large and somewhat clumsy; he had a thundering voice, and piercing eyes that were startling even in old photographs. The conventional role of the intellectual did not appeal to him … He was not inclined toward modesty … [His] energy and ambition have been described, with only slight exaggeration, as volcanic. In nine years at McGill … he managed to publish some seventy papers, become a Fellow of the Royal Society, build a significant research school, and complete the research that later earned him a Nobel prize.

But he was not above criticism from his fellow faculty members. Some feared that he was discrediting McGill by propounding radical ideas about such a ridiculous thing as spontaneous transmutation; others urged him to delay publication. Fortunately, his physics department chairman, John Cox, supported him unreservedly, and even voluntarily filled in for his teaching duties to allow him more time for research (6).

He was once told, as he was preparing a broadcast from Canada to England, that he did not need a microphone. His voice resounded throughout the building, often accompanied by his favorite off-key tune, "Onward Christian Soldiers…" if he were in a good mood. He would daily visit, some said "patrol," each student or collaborator, always looking for, some said "demanding," results or making suggestions, many of which led to fruitful outcomes. His insight into problems was called "visionary," "uncanny," "an inner light." He is said to have been able to pay attention not so much to what Nature was saying, but to what Nature was whispering (7).

For those who had the temerity to cross him, he was unforgiving, as we have seen in his reaction to the departmental space crisis at his new academic home in Manchester. On the other hand, when Henry G. J. Moseley (1887-1915), a "mere 25-year old demonstrator" working under him there dared to point out a series of mathematical errors Rutherford had made on the origins of beta rays, he humbly admitted his error: "Mr. Moseley drew my attention to the fact, which I had overlooked, that according to the Lorentz-Einstein theory…" appeared in the December 1912 issue of *Philosophical Magazine* (8).

Another characteristic, alluded to in Part I, was his reading habits. His wife was witness to his insatiable desire to read as much as possible and whatever was to hand, whether it be novels, history, biographies, and occasional murder mysteries. The McGill librarians had a difficult time keeping up with his needs, and they could not foist off books already read—his content retention was prodigious (9). It was this habit, along with his enjoyment of bridge and a game of golf, that allowed his fertile mind to lie fallow on a regular basis, and as in agriculture, this was a method to generate even more ideas at a future date. In fact, reading, and especially fiction, is an admirable way of developing one's imagination; the reader is forced to absorb the descriptions from the written word and create one's own space and time. And there is no doubt that Rutherford's incredible imagination was what enabled him to look inside the atom and describe what he saw to the outside world.

Another side to Rutherford that is often not mentioned was his support and encouragement of women in the sciences. He has been lauded as the "key figure" in the British radioactivity group. His first graduate student was Harriet Brooks (1876-1933) followed by at least a half dozen other women. He was among the first proponents of opening up Cambridge to women as well (10). In addition, this attitude seems to have rubbed off on some of his collaborators, principally Frederick Soddy, who had long-term mentoring and collaborative relationships with a number of women (11).

Rutherford was also frugal, perhaps to a fault, but born of necessity. His watchword was often quoted: "We have no money, so we have to think." His experimental apparatus was often drawn from things that he had to hand. An inveterate smoker, he used discarded cigarette tins for a number of purposes. Balls of string and the proverbial "sealing wax" were always available, and virtually every piece of equipment was made by himself or a few of his assistants until well on into his career. And even then, with special needs and purposes, his tools were made of glass and brass, and hardly anything more. His most expensive material consisted of radioactive sources like radium and thorium, and even these were, for the most part, "on loan" from other institutions. Figure 1 is a photograph of his 1920s Cambridge laboratory, an icon of

frugality. Although Rutherford could have commercialized some of his discoveries, he never did so. Nor did he ever seek or receive money from patents, inventions or discoveries, although he was always delighted to receive a raise in salary or prize money from his many awards (12).

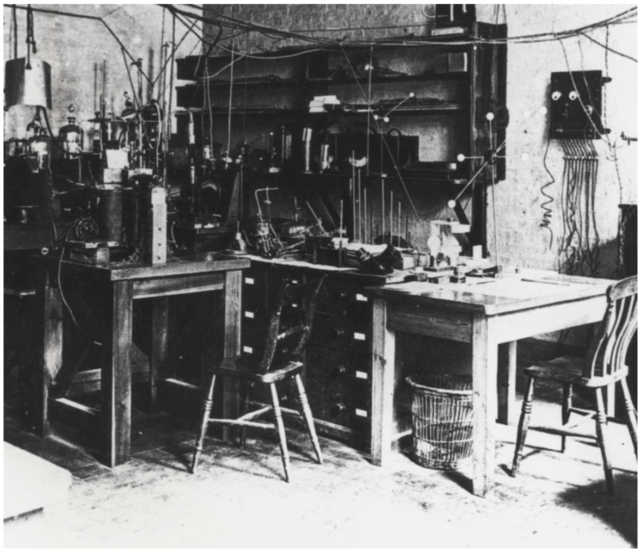

***Figure 1**. Rutherford's research room at Cambridge, 1920s. (Science Museum London / Science and Society Picture Library, https://commons.wikimedia.org/wiki/File:Sir_Ernest_Rutherfords_laboratory,_early_20th_century._(9660575343).jpg, Creative Commons Attribution-Share Alike 2.0 license)*

Victoria University, Manchester (1907-1919)

We have seen that Rutherford's entrance onto the scene at Manchester was not exactly unobtrusive. His future activity there was to become legendary. Situated at last near the world's scientific center of gravity, Rutherford quickly *became* that center. In addition to large numbers of graduate students that soon stretched the limits of the university's physics facilities, he also began to attract brilliant physicists as postdoctoral collaborators, many destined to become Nobel laureates in their own right in years to come. Among the most notable were Niels Bohr (1885-1962), Georg von Hevesy (1885-1966) and James Chadwick (1891-1974). In addition, he "inherited" a research assistant, Hans Geiger (1882-1945) and a most superb glassblower, Otto Baumbach (1882-1966), without whose expertise the atomic nucleus might never have been discovered. Two of the most famous undergraduates also worked with Rutherford at Manchester, Ernest Marsden (1889-1970) and Henry G. J. Moseley.

One other great boon to the university was Rutherford's ability to procure radioactive samples of pitchblende from the Curies and a precious 300 mg of radium chloride, on loan, from the Radium Institute of Vienna. The latter acquisition came only after a fairly contentious correspondence with William Ramsay (1852-1916), working in London, who received 350 mg of radium bromide from the Institute with the condition that he share it with Rutherford—but it turned out not to be share and share alike. Ramsay proposed to keep the source for over a year before sending it on to Manchester, which was unacceptable to Rutherford. Fortunately, the impasse was resolved by the second loan.

One of the first projects Rutherford took up when he arrived in Manchester in May 1907, was the persistent question of the nature of the alpha particle. He was convinced that this mysterious entity was helium, but he needed to prove it. Working with Geiger, the two succeeded in observing the multiplicative ionization effect of individual alpha particles by firing them into a tube containing a wire held at very high voltage. The entry of the particle causes the wire to discharge; it is quickly recharged by a supplementary source so as to be ready for the next alpha particle. By this method, they found that a gram of radium expels 3.4×10^{10} alpha particles every second (13). The apparatus itself was eventually refined and developed into the famous Geiger counter, a standard piece of equipment for measuring radioactivity quantitatively. They had obtained their results by late January 1908, and the paper was read to the Manchester Literary and Philosophical Society on February 11, 1908 (14). Knowing the number of particles discharged from the radium, this experiment enabled Rutherford to definitely assign the charge on the alpha particle: a positive charge about twice the magnitude of the negative charge on the electron (15).

Still in hot pursuit of the nature of the alpha particle, and taking advantage of Baumbach's skill, Rutherford, working with post-graduate student Thomas Royds (1884-1955) (16), designed a glass apparatus with an inner tube and an outer tube. The inner tube, into which he would place his sample of radium emanation, had to have an extremely thin wall, less than 0.01 mm thick, that would allow energetic alphas to escape, but retain the parent emanation (radon) atoms that were their source. The outer tube that surrounded the emanation tube was exhausted by a pump and then (17)

> completed by means of a charcoal tube immersed in liquid air. By means of another side tube connected with a mercury reservoir, the gases formed within the outside tube could be compressed into a small vacuum tube attached to the top and their spectra examined.

The experiment began by pumping "emanation" gas into the inner tube and evacuating the outer cylinder as just described.

> Twenty-four hours after the introduction of the emanation, no trace of helium was detected on compression of the gases into the vacuum tube; at the end of two days, the helium yellow line was seen faintly; after four days, the yellow and green lines came out brightly, and after six days practically the whole helium spectrum was observed.

A second experiment was necessary to find out if the helium could have diffused from the emanation through the thin glass wall of the inner tube. To accomplish this, the entire experiment was run again, but this time by filling the inner tube with elemental helium alone. No trace of helium was observed in the outer tube over a period of eight days. Emanation was then placed in the inner tube once more, and after four days, the helium spectrum was again observed in the outer tube (18).

This stupendous achievement, later dubbed "The Beautiful Experiment" (19), was communicated to the Manchester Literary and Philosophical Society on November 3, 1908, and five days later the following headline (Figure 2) appeared in the *New York Times* (20).

ATOM OF MATTER CAN BE DETECTED

Prof. Rutherford, Expert on Radio-Activity, Makes Successful Experiments.

SUBSTANCES TRANSFORMED

Accomplished by Expulsion of an "Alpha Particle," Which Prof. Rutherford Believes Is an Atom of Helium.

Special Cable to THE NEW YORK TIMES.

LONDON, Nov. 7.—Prof. Ernest Rutherford, Director of the physical laboratories at Manchester University, and one of the world's foremost authorities on radio-activity, details in a communication addressed to The Scientific Weekly the nature of certain experiments which, in addition to important results from the point of view of radio-active data, are noteworthy from the fact that during their progress it was for the first time possible to detect a single atom of matter. This can be done in two ways, one electrical and the other optical.

***Figure 2**. A special cable dispatch to the* New York Times *reporting on Rutherford and Royds's experiment (20).*

Of course, the most important part of the communication was the nature of the alpha-particle, which seemed to get obscured in "reporter-ese." Perhaps the phrase "believes is an atom of helium" should have read "proved it is an atom of helium."

Essentially, Rutherford's experimental design was able to show that "helium could be obtained from accumulated α particles, quite independently of the active matter from which they are expelled" (17). A ten-year long conundrum was finally solved through the great expertise of a technical glassblower and the workings of an ingenious mind.

This achievement may have put a period to a banner year, but the year had about seven more weeks to run and within a day of his α particle communication, he received a telegram from Stockholm informing him that he was the 1908 Nobel laureate in chemistry "for his investigations into the disintegration of the elements, and the chemistry of radioactive substances" (21). This was for the work he had done at McGill prior to his move to Manchester.

A little over a month later, December 10, 1908, Ernest and Mary Rutherford arrived in Stockholm, and his Nobel medal was presented by the King of Sweden on the following day. Rutherford confessed that the award was unexpected, and that the most startling aspect was his quick metamorphosis from a physicist into a chemist (22). In the afternoon of December 12, he delivered his 5000-word Nobel lecture, "The Chemical Nature of the Alpha Particles from Radioactive Substances," a retrospective tutorial that briefly described his published work beginning in 1899 when alpha particles were first observed as a special type of radiation. Toward the end, he describes his latest find (13):

> We have seen that there is every reason to believe that the α-particles, so freely expelled from the great majority of radioactive substances, are identical in mass and constitution and must consist of atoms of helium.

And he concludes with a question regarding future investigations:

> On this view, it may prove significant that the atomic weights of many elements differ by four—the atomic weight of helium—or a multiple of four. Time is too limited to discuss in greater detail these and other interesting questions which have been raised by the proof of the chemical nature of the α-particle.

In the *New York Times* article cited above, mention is made of two ways of counting atoms of matter, electrical or optical. The optical method had been discovered by Sir William Crookes (1832-1919) in 1903. If radiation emitted by a radioactive substance struck a plate covered by a phosphorescent substance such as zinc sulfide, flashes, or bright points, called scintillations, could be observed. Rutherford and Geiger found that this phenomenon could be turned into a precise and convenient laboratory method for counting single particles.

They began by using the alpha particle as a tool to examine its interaction with matter. A sharp image can be obtained on a photographic plate by focusing a well-defined narrow unobstructed beam of alpha particles onto it. However, if a very thin sheet of metal is placed between the beam and the plate, the image becomes diffuse, and the thicker the sheet, the even more diffuse the image. They attributed this scattering effect to multiple interactions of the alpha particles with the atoms in the metal sheet, skewing them slightly from their straight line course. The thicker the sheet and the higher the atomic weight of the metal, the greater the number and impact of interactions taking place, and consequently, the more broadening out of the image. This explanation is very plausible if one visualizes the aggregate of atoms in the sheet as a grid consisting of alternate and evenly spaced positive and negative charges.

In 1908, Geiger decided to use Crookes's scintillation method to measure the scattering effect. In an evacuated system to prevent scattering by air, he guided a beam of alpha particles from a lead chamber that contained the source element through a narrow slit and allowed the beam to fall on a zinc sulfide phosphorescent screen. Without an obstacle to divert their travel, the scintillations observed exhibited no deviation from the expected straight-line paths of the alpha particles. Introduction of a thin metal foil between the slit and the screen produced scintillations corresponding to the particles' departure from a straight line. The scintillations could be counted to measure the degree of scattering; very few particles were scattered through large angles, as expected. Also, not surprisingly, the extent of scattering increased both with the thickness of the foil and the atomic weight of the metal (23).

One fine day in May 1909, Geiger suggested that the 20-year old undergraduate, Ernest Marsden, be given a research project of his own. Always thinking outside the box, Rutherford suggested that he devise an apparatus that would allow him to observe and measure alpha scattering at large angles, if any. Rutherford knew that the multiple scattering model would predict no large deflections. The apocryphal story line tells us that Geiger returned excitedly to Rutherford a few days later to say that they had viewed alpha particles shooting backward, a most incredible event. They commented in their first paper (24):

> If the high velocity and mass of the α-particle be taken into account, it seems surprising that some of the α-particles, as the experiment shows, can be turned within a layer of 6×10^{-5} cm. of gold through an angle of 90°, and even more. To produce a similar effect by a magnetic field, the enormous field of 10^9 absolute units would be required.

These last few words hint at the immense force field that the α-particles were encountering in their journey.

However, to build the elaborate apparatus to accomplish this would take more than just a few days (Figure 3) because the viewing microscope would have to be rotated through some large angles while maintaining an unbroken vacuum. The heart of the system was a strong metal box, B, containing the radioactive α-source, R, the scattering foil, F, the microscope, M, and the ZnS screen, S. The ground glass plate, P, seals the box, which is then evacuated through the tube, T. A fine pencil of particles is directed through the aluminum diaphragm, D, onto the foil, F. and scintillations are observed on the screen. Observations can be made through a wide range of angles by rotating the box-microscope-screen unit about the airtight joint, C, while the rest of the apparatus remains fixed in place attached to the tube, T. Geiger and Marsden were able to take measurements between the angles of 5° and 150° over the course of several weeks, but there was too much interference from β and γ radiation to take data at greater angles. They also varied the composition and thickness of the foils and published detailed tables of their results in 1909, with more elaborate work and details of the apparatus later, in 1913 (25).

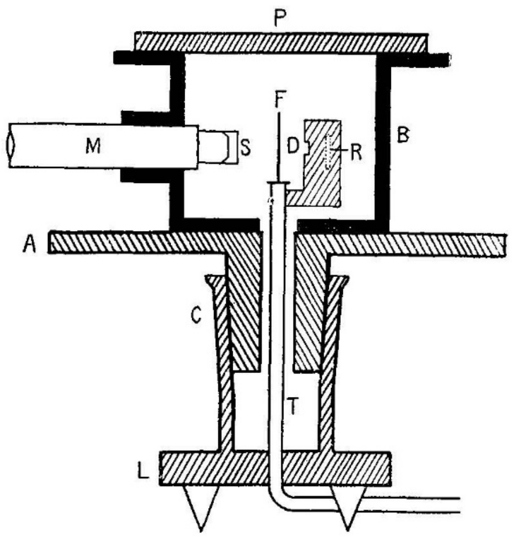

Figure 3*. The Geiger-Marsden apparatus for measuring large alpha particle scattering angles* (25, p 607).

The New England poet, Emily Dickinson (1830-1886), exhorted Nature to "tell all the truth, but tell it slant," so that our poor brains must ponder meaning, concluding that "the truth must dazzle gradually, or every man be blind" (26). Yes, truth dazzles! But not immediately. Rutherford pondered and pondered the truth of the scattering experiments for over a year. He even went back to school, sitting in on undergraduate statistics classes, so that he could begin to fathom what in his heart he already knew (27). That alpha particles traveling at 10,000 miles per second could be diverted backwards from their trajectory by a flimsy sheet of metal was beyond belief. He realized and expressed the analogy that it was like firing a bullet at a piece of tissue paper and having it bounce back at you. And gradually … he understood. He realized that there was no such thing as multiple encounters to explain scattering at large angles; the statistics simply did not work because the probability of such an event was infinitesimally small. But Geiger and Marsden showed that such an event happened, on average, every 1 in 20,000 times, a small but significant occurrence. Alpha particles traveling at that speed had to be experiencing single encounters—but with what? Rutherford put it very elegantly in his landmark paper on the subject (28):

> It seems reasonable to suppose that the deflexion though a large angle is due to a single atomic encounter, for the chance of a second encounter of a kind to produce a large deflexion must in most cases be exceedingly small. A simple calculation shows that the atom must be a seat of an intense electric field in order to produce such a large deflexion at a single encounter.

Malcolm Longair, a renowned astrophysicist and historian of the Cavendish Laboratory, follows up on Rutherford's qualitative description with this remark (29):

> Rutherford was notoriously skeptical of theory, but on this occasion he worked out the formulae for what became known as *Rutherford scattering* himself. In particular, he predicted the angular distribution of the α-particles.

It took quite some time and more experiments before the nature of the "intense electric field" could be enlarged upon. It took even longer for the term "nucleus," coined by Rutherford, to take hold. His first published use of the term "nucleus" when referring to the internal structure of the atom appeared in 1912 in an article in the *Philosophical Magazine* (30):

> In a previous paper I have given reasons for believing that the atom consists of a positively charged nucleus of very small dimensions, surrounded by a distribution of electrons in rapid motion...

In 1913 in his third book, *Radioactive Substances and Their Radiations*, he mentions some of those reasons (31):

> To account for the experimental results, it is necessary to suppose that the atom is the seat of such intense electrical forces that occasionally the α particle can be deflected from its path through more than a right angle in an encounter with a single atom. This indicates that an atom must contain a highly concentrated charged nucleus, and that the α particle in passing through the atom close to the nucleus suffers a wide deflection of its orbit.

Later calculations showed that the size of this charge should be of the order of 10^{-13} cm, which raised some additional serious questions regarding the positions of the electrons and the actual size of the entire atom.

James Chadwick, who was, in 1932, to discover the neutron intuited by Rutherford in 1920 (32), put it this way (33):

> The genius of Rutherford has seized upon an apparently unimportant detail and transferred it into a clue to the problem of the inner structure of the atom. The nuclear theory of the atom was published in a surprisingly complete form in the same year [1911]. Supported at first by the preliminary experiments of Geiger on the variations of the scattering with angle, it was in the next few months confirmed in its minutest details by a beautiful series of accurate, quantitative tests. It would be difficult to exaggerate the influence of the nuclear theory of atomic structure on the whole range of the exact natural sciences. The theory will

> surely rank as the greatest of all Rutherford's contributions to physics.

But the truth must dazzle gradually. Surprisingly, this epochal discovery was met with indifference on the part of both scientists and the general public. Apparently, even Rutherford was not aware of the enormous implications until much later (34).

And meanwhile, life in the Manchester laboratory carried on. Rutherford was constantly on the move, giving lectures, accepting new honors, deeply engaged in the service of several prestigious scientific societies, and managing the large number of researchers that his reputation attracted. In 1914, he found time to do an elegant piece of work with his collaborator and, later, biographer, Edward N. da Costa Andrade, on the nature of gamma rays. Using crystalline mica as a type of diffraction grating, they were able to discern the bright lines and dark lines that signaled constructive and destructive interference typical of electromagnetic radiation. By measuring the angles at which the gamma rays were deflected, they were able to calculate their frequencies and found that they were similar to X-rays with more of them toward the high energy end of the spectrum (35, 36). It was later realized that gamma rays and X-rays share very similar properties, but different origins. Gamma rays arise out of the energy changes taking place in the nucleus of the atom; X-rays arise from energy changes in the extranuclear electrons.

1914 was also the year that brought a great change in the pace and purpose of life at the university and in the rest of the country. On July 28, while Rutherford and his wife, and Henry Moseley and his mother, were traveling to Australia to attend and present at the British Association for the Advancement of Science meeting in Melbourne, war broke out. Although the meeting was not affected, by the time that Rutherford returned to England, the whole world had been turned on its head. Moseley headed straight home to enlist, and would shortly die by a sniper's bullet in the Dardanelles. Chadwick, who had been doing research in Germany was interned there as an enemy civilian. Many of Rutherford's own collaborators, including Andrade, were already inducted into the army. Marsden departed in 1915 to take up a professorship in New Zealand. And the whole laboratory shut down its normal activities to engage in war work. Rutherford himself, relying on his expertise and experience on long-distance transmission of waves, spent enormous amounts of time working on submarine detection devices, later called SONAR (37). During the war years, with his staff very much depleted and his time taken up with war work, Rutherford did not publish very much: two papers, amounting to 18 pages in toto, was his output for 1917 and 1918.

With the end of the war on 11 November 1918, things geared up again in the laboratory. Prior to his departure, Marsden had been investigating the interaction of α particles with hydrogen and found that he could treat them like a game of marbles: when the α particles struck hydrogen molecules, they flew off much farther than their normal range (38). Rutherford used this knowledge as a stepping stone to yet another spectacular discovery. He began by examining the effects of α- particles passing through various gases. When measuring the magnetic and electrostatic deflection of hydrogen atoms bombarded by α-particles, he found that the agreement between the calculated and observed velocities of the H atom showed that the conservation of momentum and energy hold for close collisions between atomic nuclei, i.e., there is no observable energy loss due to radiation (39, 40). In his next paper, dealing with the bombardment of nitrogen and oxygen with α-particles, he stated that the effects produced were very similar to those produced in hydrogen (41). However, when it came to bombarding nitrogen nuclei, he was astounded to note that even though nitrogen was comparatively very heavy, many long-range particles were among the products. He was able to identify the latter as hydrogen nuclei, which he later named protons, because of their behavior in a magnetic field. If there was no hydrogen present, where did they come from? There seemed to be only one answer: a chip off the old block of a nitrogen nucleus. In his own words (42):

> From the results so far obtained it is difficult to avoid the conclusion that the long-range atoms arising from collision of α particles with nitrogen are not nitrogen atoms but probably atoms of hydrogen, or atoms of mass 2. If this be the case, we must conclude that the nitrogen atom is disintegrated under the intense forces developed in close collision with a swift α particle, and that the hydrogen atom which is liberated formed a constituent part of the nitrogen nucleus.

But the next question was: how did that come about? Did the α particle knock it off as it flew by, or did the α particle first combine with the nitrogen nucleus, forming an unstable intermediate, that then exploded, sending a proton flying off at high speed? In any case, because there were changes in atomic number (43), new elements were being formed. The possibilities can be put into equations as (44):

(1) ${}_{7}N^{14} + {}_{2}He^{4} \rightarrow {}_{2}He^{4} + {}_{1}H^{1} + {}_{6}C^{13}$

(2) ${}_{7}N^{14} + {}_{2}He^{4} \rightarrow {}_{9}F^{18} \rightarrow {}_{1}H^{1} + {}_{8}O^{17}$

The first possibility involves three products, and the second only two products. This important work was done right at the time that Rutherford was preparing to leave Manchester for Cambridge. While the reality of this extraordinary event could not be called into question, the resolution of the mechanism of this reaction would have to wait for another five years. It would also set the direction of Rutherford's scientific activity for the rest of his life.

Return to Cambridge (1919-1937)

In April of 1918, J. J. Thomson was appointed Master of Trinity College, Cambridge, a duty superimposed on his directorship of the Cavendish Laboratory. The latter had been badly affected during the war: most students were recruited or volunteered for military service, the budget was cut, the laboratory space was requisitioned as an officers' billet, and in all of this, Thomson was feeling his way in uncharted waters. So, exactly one year later, he decided to step down from his post at the Cavendish and accept a professorship without a stipend. Rutherford's appointment to fill his shoes was almost a reflex reaction on the part of the powers-that-be, but Rutherford himself first contacted Thomson to make sure that they could happily coexist in an atmosphere of cordially agreed-upon division of labors. There was also a matter of salary. It was known that Rutherford was the highest paid professor in the country, and the Cavendish stipend could not match what he was already earning. True to form, not long after his appointment to the position, Thomson made sure that he was elected a Fellow of Trinity College, thus rendering an honor denied to him 21 years earlier as well as topping off his salary so that he could afford to make the transfer.

Rutherford finished out the 1919 academic year at Manchester, where his colleagues bade him a sad farewell, and he was welcomed joyfully with song and festivity to his new bailiwick in Cambridge. With him came most of his home-made equipment—simple enough, but time-consuming to replace—along with his precious radium supply, still on loan from the Vienna Institute of Radium. At 47 years of age and at the top of his form, Rutherford had to face some unprecedented challenges: finding room for the surge of students, after a four year hiatus, who wished to study physics; finding the budget, equipment, and space to accommodate them; rebuilding the infrastructure, support services, research program and curriculum that would restore the Cavendish to its premier place among British academic institutions. The University itself was of a different mind and told Rutherford that he had to raise the funds independently, which he was loath to do. Despite this, talent accompanied or came to find him. Chadwick, back from his prisoner-of-war stint in Germany, broken in health, spirit and pocketbook, was taken in by Rutherford and transferred with him to Cambridge to become his closest collaborator and eventually, assistant director of the Cavendish. Another find was Patrick Maynard Stuart Blackett (1897-1974) who, analogous to the α particles that turned about-face upon encountering an enormous force field, did the same thing on meeting the human "force of nature," Rutherford. Blackett had seen military service during the war and came to Cambridge for an officers' retraining program

***Figure 4**. Main entrance to the Old Cavendish Laboratory, Free School Lane, Cambridge (left); C. T. R. Wilson's Cloud Chamber (right) at the Museum in the New Cavendish Laboratory, Madingley Road, Cambridge. Wilson invented the cloud chamber in 1911. He realized that if the chamber is expanded just after a charged particle has passed through, then all the ions produced still lie along the path of the particle which is made visible by a row of water droplets. Both photographs: Mary Virginia Orna*

but abruptly gave up his commission to study physics as an undergraduate. When he finished in 1921, he stayed on as a research student with Rutherford and did spectacular work with the cloud chamber that was devised by C. T. R. Wilson (1869-1959). The chamber could display the tracks that charged species made when traversing the supersaturated water vapor contained therein. In 1924, examining the conundrum presented by Equations 1 and 2 (above), Blackett saw only two tracks. This meant that the α particle was actually consumed in the reaction, showing that a reaction intermediate did indeed form and that there were two final products, a proton and a new isotope of oxygen with a mass of 17 (45). These experiments demonstrated artificial transmutation by atomic bombardment. Displaying both great patience and supreme experimental skill, he took and analyzed some 400,000 particle tracks from 23,000 photographs of α particle interactions, and found 8 doubly branched tracks showing the existence of only two product particles. Years later, in the early 1930s, Blackett, working with Giuseppe (Beppo) P. S. Occhialini (1907-1993), confirmed the discovery of the positron (46). In 1948, Blackett received the Nobel prize in physics for "his improvement of the Wilson cloud-chamber method and for the resulting discoveries in the field of nuclear physics and cosmic rays" (47). Figure 4 shows the building and the apparatus that accomplished Blackett's confirmation of Equation 2.

Under Rutherford's direction, the Cavendish became a beehive of activity, but much of it was not directly related to his own research interests. Rutherford was, by now, a scientist of international proportions and this very fact often drew him away from the laboratory for months at a time. He was constantly being invited to speak, to preside at the opening of new laboratories, or to receive honors and honorary degrees at any number of institutions. Several very important honors came his way while at the Cavendish. The first in 1920, was the singular honor of being appointed for the second time by the Royal Society to deliver the Bakerian lecture. While in his first Bakerian, he spoke of spontaneous transmutation of the elements, in this he spoke of artificial disintegration of the nucleus by external forces. He also made some really astonishing predictions: the possible existence of a heavy hydrogen atom with a mass of two (deuterium), and of a lighter helium atom with a mass of three, and most prescient of all, a particle of mass one with a zero nuclear charge. The neutron was discovered by Chadwick only twelve years later. In 1923, he presided over the British Association for the Advancement of Science, in 1925 he received the Order of Merit (O.M), possibly the most prestigious British award, whose membership was limited to 24, and in 1925 he was elected to a five-year term as President of the Royal Society. In 1930, he was raised to the peerage as Lord Rutherford, First Baron Rutherford of Nelson and Cambridge (48). During these years, his travels took him to Canada, New Zealand, Australia, South Africa, and to many countries on the European continent.

Meanwhile, physics as a discipline was marching on and changing its appearance as it went. Rutherford's major contribution was in experimental physics, and gradually it was becoming apparent that theory was to be the most important handmaid that would propel the discipline well into the 21st century. The move away from simple home-made equipment, such as Francis William Aston's (1877-1945) original mass spectroscope, to the large, expensive pieces of equipment characteristic of "big science" was taking place before his eyes, and he approved. Among these changes, the work of Edward V. Appleton (1892-1965) in astrophysics and of Pyotr Kapitsa (1894-1984) in high powered magnetic fields and cryogenics were highlights in the history of the Cavendish.

Although many of the activities at the Cavendish were ancillary to Rutherford's immediate interests, the work of two young men, John Douglas Cockcroft (1897-1967) and Ernest Thomas Sinton Walton (1903-1995), traced a direct line from the early transmutation experiments to the threshold of "big science." Cockcroft, a Yorkshireman, a seasoned war veteran and electrical engineer, came to Cambridge for advanced study in his field but found Rutherford, as a mentor, irresistible. Walton, a graduate in hydrodynamics fresh from Trinity College, Dublin, was likewise drawn into the great man's force field. From 1927 until 1932, the three of them worked together to build an apparatus that would send protons barreling into resistant nuclei with enough force to split them. The goal was to obtain a continuous voltage that would be powerful enough to accelerate protons to an energy of 800,000 volts. To do this, they used large capacitors and thermionic valves to produce an alternating voltage of 200,000 volts. They knew that they were in a race with the American team in California under the direction of another Ernest, E. O. Lawrence (1901-1958), who was building his famous cyclotron.

Producing protons by ordinary electric discharge at the top of a long metal tube, Cockcroft and Walton were able to accelerate them to strike a lithium target at the bottom of the tube and detected their hoped-for products,

alpha particles, by the old tried-and-true scintillation method. The reaction that they clearly observed was

(3) $_1H^1 + {}_3Li^7 \rightarrow 2\ {}_2He^4$

What they also calculated was that the alpha particles emerged with greater energies than the incident protons, a phenomenon that would seem to contradict the Law of Conservation of Matter and Energy unless one took into account that there was considerable mass loss in this reaction. This amount was determined by the precise atomic mass measurements made by F. W. Aston. The mass loss accounted for the extra energy of the alpha particles, thus confirming Albert Einstein's (1879-1955) mass-energy relationship, $E = mc^2$. This work garnered yet another Nobel Prize for the Cavendish in 1951 "for their pioneer work on the transmutation of atomic nuclei by artificially accelerated atomic particles" (49).

Meanwhile, Rutherford continued his grueling pace of lectures, conferences, Royal Society duties, and writing right on up to the year he died. In 1933, he took on yet another unprecedented task at the urging of his friend, Albert Einstein, who was deeply and personally affected by the rise to power of the Nazis in Germany. By that year, thousands of personnel from German universities and other institutions of higher learning had been dismissed from their jobs and forced to flee for their lives. Many of these refugees, some of great academic standing, were already in England, jobless and penniless. Rutherford took the helm of the newly formed Academic Assistance Council, raising funds on its behalf and finding jobs for many of those affected by Germany's persecution, and as the years went by, the situation became worse and worse.

In 1936, Rutherford delivered the prestigious Henry Sidgwick Memorial Lecture, and a modified version of his talk was published in the summer of the following year called *The Newer Alchemy* (50). It was to be one his last publications. In mid-October 1937, he suffered a fall while doing some garden work at his home, and a few days later, on 19 October, he passed away unexpectedly from what has been described as a "strangulated hernia." There was a period of national mourning for this great figure of science whose ashes were eventually interred with great honor in Westminster Abbey.

Ernest Rutherford's Legacy

Aside from his most outstanding personal quality, honesty, that informed his dealings with others, with his science, and with his own self-assessment, he was quite without affectation, self-consciousness, or pretentiousness of any sort (51). Though not a chemist, he was the first to transmute one chemical element into another. Though not a geologist, he was the first to reliably determine the age of the earth. Though educated as an experimental physicist, he raised this discipline to new heights and spawned several more: atomic physics, nuclear physics and nuclear engineering. Though an experimentalist at heart, he embraced the conclusions of quantum physics to explain many observed properties of his nuclear atom, all derived by his good friend and protégé, Niels Bohr. Though not a theorist, his splitting of the atom confirmed Albert Einstein's famous mass-energy relationship.

His three major accomplishments, in chronological order were:

- Discovery of spontaneous transmutation of the atom, its nature and mechanism, its timeline, its energy quotient
- Discovery of the atomic nucleus
- Artificial transmutation with alpha particles and later with accelerated protons

Though he only won one Nobel prize, all three of these accomplishments were deserving of that award.

In addition, he fostered and was in close association with those who:

- Discovered the organizing principle of the periodic table, atomic number—Henry G. J. Moseley
- Discovered that proton number and neutron number of the nucleus were independent (existence of isotopes)—Frederick Soddy
- Formulated Soddy's Displacement Law—Alpha particle emission yields a new nucleus with an atomic weight of four less and an atomic number of two less than the original nucleus; beta emission yields a new nucleus with the same mass but an atomic number of one greater than the original nucleus
- Discovered the neutron—James Chadwick

Furthermore, long before they were discovered he predicted the existence of:

- Heavy hydrogen (deuterium)
- The neutron
- Helium with a mass number of 3

And although he does not universally get the credit, he discovered the element radon, which he called "tho-

rium emanation" about a year before the other emanations (isotopes) of radon were discovered.

Since Rutherford made major contributions to the formation of the modern periodic table, he certainly deserves a place, as rutherfordium (atomic number 104) in this most exclusive club in the world.

Acknowledgments

To Steve Martin, Cavendish Laboratory, Cambridge for invaluable help and information; with deep appreciation to the Editor of this journal, Carmen Giunta, and to the anonymous reviewer whose comments, suggestions and criticisms have greatly enhanced this paper.

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44. The subscripts denote the number of protons, the superscripts denote mass number (protons and neutrons), the sums of the superscripts and subscripts must be equal on both sides of the equation. Rutherford would not have been able to write these equations because, as yet, the neutron had not been discovered.

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THE IODINE INDUSTRY IN GLASGOW AND SCOTLAND

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Introduction

For most of the 19th century and well into the 20th century, Glasgow was the UK center for the iodine industry, together with other nearby Scottish lowland towns. Iodine was obtained from seaweed, a renewable resource, which was harvested on the coasts of Scotland and Ireland. It was burnt to produce kelp (the vitreous ash from burnt seaweed), and much of it was shipped into the Clyde, first for Glasgow's soap and glass works and later for the production of potash (manure) and iodine. In the middle to late 1800s Glasgow produced 90% of the UK's iodine and a substantial proportion of the world's supply. The death-knell of the industry was the first importation of iodine from Chilean caliche in 1874, and this supply of iodine grew and eventually dominated world supply, as it was more abundant and easier and cheaper to produce. The Chilean nitrate industry could produce up to 5,100 tons of iodine a year as a by-product of nitrate production at a time when world demand was only 500 tons. The production of iodine from kelp limped on, thanks to an international iodine cartel to regulate prices (1), until 1931 when the last iodine factory in Glasgow closed. In an earlier article I gave a general survey of the kelp and iodine industry in Ireland (2).

We can identify several phases in the chemical utilization of seaweed (dates are approximate). This article will focus on phase 2 in Scotland.

Phase 0: Use of seaweed directly as a green manure (<1700 to today)

Phase 1: Production of kelp as a source of alkali (soda) (~1700 - ~1840)

Phase 2: Production of kelp for iodine and potash (1811 - ~1940s)

Phase 3: Extraction of alginates (1881 - present)

Phase 4: Use of seaweed for food, fuel, fertilizer, cosmetics etc. (largely post 1950)

The important roles of kelp were as a source of soda (Phase 1), which lasted for over a century, and then for potash and iodine (Phase 2). Kelp was superseded by cheaper mineral sources of these products by the 1880s. Alginates have since become the lifeblood of the seaweed to chemicals industry (Phase 3), following their discovery and isolation by Stanford in the 1880s (3). Interestingly seaweed is still harvested and used directly as a green manure (Phase 0) and the contemporary use of seaweeds (Phase 4) is thriving, with its sustainable and green credentials.

Edward Stanford, who was an important manufacturer in the Glasgow iodine industry from 1863 onwards, identifies "Glasgow, to which city or its district the manufacture of British iodine has always been confined" (4). This reinforces the importance of Glasgow as the main center for iodine production in the British Isles,

but ignores the smaller contribution of the Irish iodine works, often linked to the Scottish manufacturers, and other smaller works in Scotland, for example in Falkirk and Borrowstouness (Bo'ness). In this article I want to trace the history of the iodine from seaweed industry in Scotland, as far as existing records allow.

Despite its obvious importance to Glasgow in the 19th century, very little has been written about this industry, apart from brief mentions. A recent article by John Christie on "Chemical Glasgow and its Entrepreneurs, 1760-1860" (5) does not mention the iodine industry and only refers briefly to the opposition by the "Kelpers," when Charles Tennant sought to introduce the LeBlanc soda process in Glasgow (6). Around 1800, kelp was the main source of soda (not potash as Christie states) for the soap, glass, alum and other industries, and it was later displaced by synthetic alkali. The British Association for the Advancement of Science (BAAS) started meeting annually in cities around Great Britain from 1831. A report was published of papers and reports from the annual meeting, and a tradition arose whereby the local industry was described. The BAAS met in Glasgow in 1840, 1855, 1876, 1901 and 1928, covering the period of the iodine industry, and in their annual Reports for 1840, 1876 and 1901 we have accounts of the chemical industry in Glasgow, including the iodine industry. These reports are referred to below and give contemporary snapshots of the iodine industry. This was small in production compared to other chemical industries, especially the alkali industry, but was still important for medical, photographic and chemical applications.

Scotland had sourced kelp, the slag of burnt seaweeds, from Ireland from the 18th century onwards, when kelp was imported for its soda content, in phase 1 of the kelp industry. The Glasgow iodine industry had strong links to Ireland and in the 1860s supplied 60% of the Glasgow demand for kelp. In addition, branch factories were set up in Ireland by Scottish manufacturers, e.g., John Ward in Ramelton, County Donegal (1845), E. C. C. Stanford in Freagh, County Clare (1878), and possibly also Edward Bullock, Galway (~1850). Scottish agents were active in Ireland for most of the 19th century and into the 20th century, buying up kelp supplies for shipping to the Glasgow factories. The reason for these ties was that Irish kelp was mostly made from deep-sea seaweeds (subtidal drift weed) and was richer in iodine than Scottish kelp (largely made from inter-tidal cut weed), and was thus worth more to iodine manufacturers. The domination of Ireland's seaweed processing industry by Scotland continued into the 20th century and most of the seaweed meal produced by Ireland's state-owned company Arramara Teoranta, based in Connemara and started in 1947, was shipped to Girvan in Scotland for the extraction of alginates until that factory closed (Phase 3 of the kelp industry). It is now owned since 2014 by a Canadian company, Acadian Seaplants. The seaweed, kelp, iodine and alginate industries of Scotland and Ireland were interlinked for over 200 years.

Chemicals from Seaweed before the Discovery of Iodine

The use of seaweed to produce kelp as a source of chemicals is much older than the iodine industry. Kelp, has been used as a source of alkali (soda) as far back as the 17th century, for the soap, glass, alum and textile industries, and production became a major enterprise in Scotland and Ireland from around 1730 onwards. From then until around 1830 it dominated the economy of the coastal regions of the Scottish Highlands and islands. It was the major source of cash income, in impoverished and subsistence areas, and because it was labor-intensive, it produced a population explosion and a neglect of agriculture. It resulted in vast profits for the landlords for a time; when it collapsed in the early 1820s, first due to competition from imported barilla (a plant-based source of soda from Spain) and then from synthetic LeBlanc soda, it led to poverty, starvation and emigration on a vast scale. Seaweed-derived kelp had been a cheap indigenous source of alkali, although barilla was richer in soda and was widely used.

Kelp production was also threatened by the development of the synthetic soda industry on a large scale from about 1823 onwards, associated with the Irishman James Muspratt and the Scot Charles Tennant. Muspratt moved from Dublin and settled in Liverpool, where he became a chemical magnate, while Tennant established the St. Rollox Works in Glasgow. Until then alkali supplies had mainly depended on foreign imports of potash (from wood ash) or barilla (from coastal plants). Kelp thus provided a local supply of alkali, with almost unlimited resources, and not surprisingly the boom years of the kelp industry occurred during the Napoleonic Wars (1790-1815), when foreign trade in potash and barilla was disrupted. At its peak kelp was worth £20 a ton and 20,000 tons were made each year in Scotland, making the landowners, but not their tenants, very wealthy (7). Each ton of kelp required at least 20 tons of wet seaweed, so this amount represents an enormous harvest, which employed tens of thousands of people, including whole

families. It was hard, wet, back-breaking work in all weathers. However, the variable composition, impurities, low alkali content and seasonal supply of kelp could not compete in the long-term with soda produced synthetically from salt, which was purer and cheaper. Some glass and soap manufacturers in Glasgow still used kelp until about 1845, probably because tradition dies hard.

The experience of Scotland and Ireland was similar but the collapse of the first phase of the kelp industry seems to have had a more dramatic effect in the highlands and islands of Scotland, where more people depended on it, than in the coastal areas of North-West and West Ireland. The industry was also linked in Scotland to the relationship between crofters and landlords, where the crofters did the hard work and made a little income, and the landlords did nothing and made large profits for several years (8, 9). The kelp was shipped from Scotland and Ireland to a wide range of end-users—industries making alum, paper, soap, textiles etc.—in Scotland and England. In Scotland Glasgow was a major center for soap-boiling and glass-making and thus a major consumer of kelp, and this helped it to become a major center for iodine production.

Discovery of Iodine in Kelp Residues

In 1811 Bernard Courtois, a French chemical manufacturer, was using kelp liquors as a source of potassium salts for making saltpeter (potassium nitrate) for gunpowder, to replace supplies from India during the Napoleonic wars. He observed corrosion of his copper pans and on adding sulfuric acid to clean them, noticed the production of a violet-colored vapor, which condensed into a blue-black solid. He sent samples to French chemists in 1812, as he hadn't time himself to research it properly. They soon realized that Courtois had discovered a new element, similar to chlorine, and details were first published in 1813 (10). It was named iodine in English by Humphry Davy, from the French name *iode*, derived from its violet color. This serendipitous discovery was to form the basis of a new industry and phase 2 of the chemicals from kelp industry. Courtois tried to market iodine from kelp without success, and eventually died in poverty, although Brittany in France became the earliest center for iodine manufacture from the mid-1820s and was the main competitor to Scotland. Iodine was first extracted in Glasgow from about 1814 onwards from the waste leys from soap boiling, marking the start of the Glasgow iodine industry, due to the chemist, Andrew Ure (11).

The discovery and chemical properties of iodine were announced in 1813, both by Courtois and later J.-L. Gay-Lussac (12), who identified it as an element, in France, and almost simultaneously by Humphry Davy in London (13). Davy had taken the opportunity, having seen samples of the new element when travelling in France, to make his own claim for priority. News of a new element spread rapidly through the chemical world and sparked off a frantic period of research worldwide, but especially in France and the United Kingdom, into the chemistry and potential uses of the new element. It was a new element with an unknown chemistry and with potential new applications. In Scotland, Ure investigated the best way for liberating iodine from kelp residues, then available in Glasgow as a waste product from soap-boiling, and would appear to have become a small-scale manufacturer (11):

> As many of the Scotch soap manufacturers use scarcely any other alkaline matter for their hard soaps except kelp, it occurred to me that in some of their residuums a substance might be found, rich in iodine. Accordingly, after some investigation, I found a brown liquid of an oily consistence, from which I expected to procure what I wanted. This liquid drains from the salt, which they boil up and evaporate to dryness from their waste leys for the soda manufacturer.

Ure describes his experiments to optimize the extraction of iodine by treating the kelp liquors with sulfuric acid and manganese dioxide (manganese(IV) oxide, MnO_2). The use of manganese dioxide as an oxidant had been suggested to him by the English chemist William Hyde Wollaston, who had also told Charles Macintosh. The method Ure described was the one adopted almost without change by the Scottish and Irish iodine manufacturers, and described later in detail by Muspratt (14) and others. Until the 1840s most of the iodine in Glasgow was produced from the waste from soap boilers, starting at step 6 in the process listed in the next section. When demand for iodine increased, many chemical manufacturers started making iodine from kelp in their own right, together with various valuable sodium and potassium salts. We are fortunate in having an account from 1840 by Professor Thomas Thomson, prepared for the 1840 BAAS meeting in Glasgow (15). It is interesting in that it states that a few years before there were as many as ten iodine manufactories in Glasgow.

From the Transactions of the British Association for the Advancement of Science, 1840.

> Glasgow being the seat of a great many interesting and important chemical manufactures, it occurred to me (said Professor Thomson) that it might be

> of advantage to those members of the chemical section, who have come from a distance, to give a short catalogue of the most important of these manufactures, that they might know what the information is which they expect, and where they are to look for it.
>
> …
>
> 9. Another chemical manufacture of considerable importance, and which the author believes to be peculiar to Glasgow, is *Iodine*. A few years ago, there were no fewer than ten manufactories, in each of which it was made to a considerable extent; but as iodine is only used in medicine, the sale is necessarily limited, and most of those works are now abandoned. The process followed by all the makers was, Dr. Thomson believes, the process of Mr. Macintosh. Iodine is made from kelp, and it deserves attention, that those kinds of kelp that contain most potash, contain, at the same time, the most iodine. The kelp is lixiviated, and all the salts which can be extracted from the solution by evaporation are separated. The mother water remaining is now mixed with an excess of sulphuric acid. A great quantity of sulphuretted hydrogen is evolved, the bad effects of which on the workmen, are obviated by setting it on fire, and allowing it to burn as it is extracted from the liquid. To the liquid thus freed from sulphuretted hydrogen, and from muriatic acid, a quantity of binoxide of manganese, equal in weight to the sulphuric acid employed, is added. The whole is put into a leaden still, and heated to a temperature which must not exceed 190° or 200° [°F] at most. The iodine passes into the receiver which consists of a series of spherical glasses, having two mouths opposite to each other, and inserted the one into the other.

Charles Glassford (16) described the state of the kelp industry in 1848 in Scotland towards the start of Glasgow's iodine industry, and he was later to be the manager of an iodine works in Galway, Ireland (17).

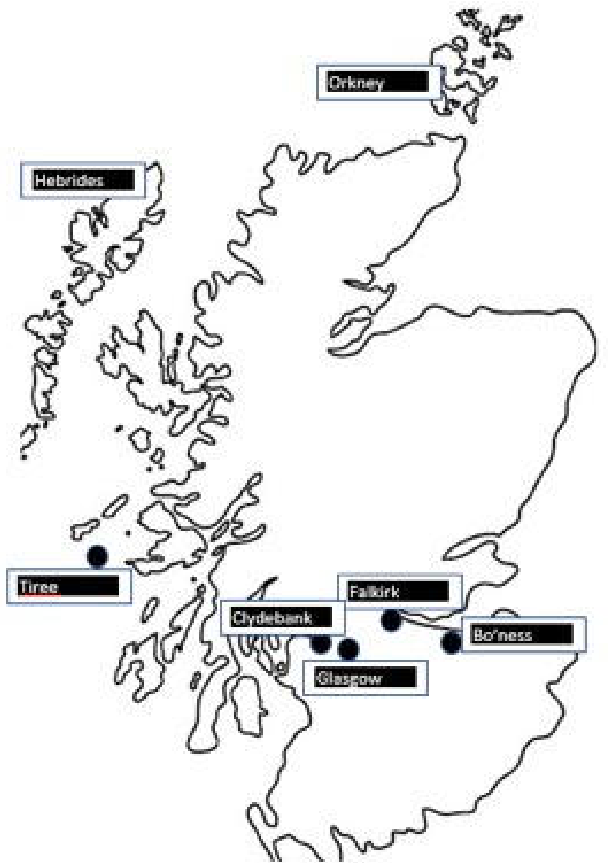

***Figure 1**. Some of the main locations for the iodine industry in Scotland.*

Figure 1 shows some of the key locations for the kelp to iodine industry in Scotland, the main location being Glasgow, where several firms were located.

The Main Extraction Process Used in Scotland

The method used by Ure was a modification of the method used by Courtois. However, instead of just using sulfuric acid (presumably fairly concentrated) as the oxidant to liberate the iodine, Ure, and most of the subsequent Scottish and Irish manufacturers, used manganese dioxide as the main oxidizing agent to liberate iodine from the iodide found in seaweed. The main steps in the extraction process are given below. From step 4 onwards the processes were done in a dedicated manufactory.

1. Collection, either from the shore or from boat, and drying of seaweed (usually in the open air in the summer). (See Figure 2.)

KELP-GATHERING ON THE WESTERN COAST OF CANTIRE.

***Figure 2**. A contemporary drawing of kelp gathering in Cantire (Kintyre) in 1861 (18).*

2. Burning the dry seaweed in simple circular or rectangular kilns on the seashore to kelp—either as a fused mass, or later as a loose ash (Figure 3).

***Figure 3**. Kelp burning on Orkney, which was a major source of kelp into the 20th century, supplying William Paterson (Glasgow) and Frederick Hughes (Bo'ness). Used by permission of Am Baile and High Life Highland.*

3. Shipping the kelp to the iodine works, usually by sea and on by canal.

4. Crushing the kelp and lixiviation (leaching) using water to extract the soluble salts, using the Shanks' system, a series of interconnected tanks for sequential extraction.

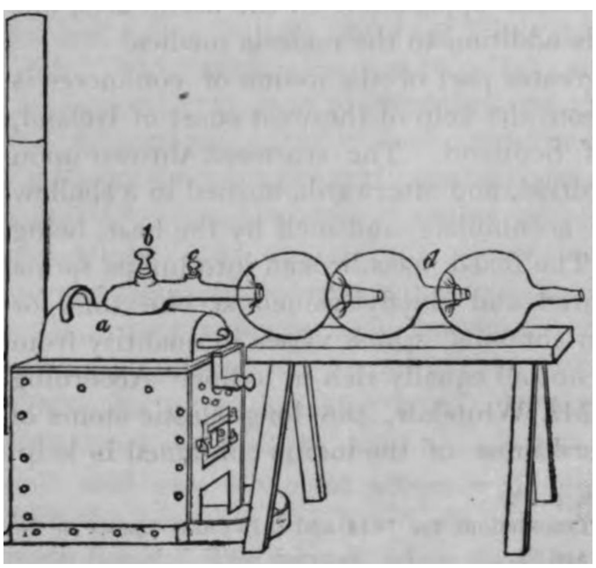

***Figure 4**. A single early iodine still, showing the row of interconnected glass udells. Often the stills and receivers were arranged in paralell banks depending on the size of the works (20).*

5. Sequential crystallization by evaporation in iron pans to obtain potassium and sodium salts.

6. Treatment of the residual liquor, containing the iodine as iodides, bromine as bromides, with sulfuric acid to remove sulfur compounds produced during burning, precipitating sulfur.

7. Heating the resultant liquor, after filtration to remove sulfur, with more sulfuric acid and manganese dioxide, in an iodine still, so that the liberated iodine distils over and is condensed (Figure 4). At first it was collected in glass vessels but later in earthenware udells (19).

8. The crude iodine was dried between sheets of blotting paper and then purified by sublimation, if necessary, in a retort such as that shown in Figure 5.

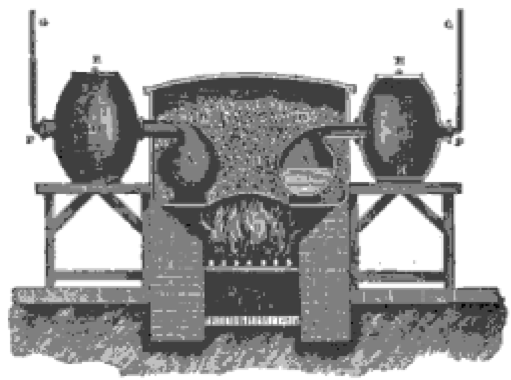

***Figure 5**. The retort used to purify iodine by sublimation (21).*

9. The iodine was packed into 1 cwt. kegs (small barrels) for shipment or converted into salts, especially potassium iodide.

10. In some works, in a subsequent step bromine was also produced, but there is only about 1/10th as much bromine compared to iodine in seaweeds, unlike in seawater.

The efficiency and productivity of this process for extracting iodine depended on collecting the most iodine-rich seaweeds, such as *laminaria digitata*, and then burning them at a low temperature to avoid loss of the volatile iodine. This was an important lesson that took the kelpers a long time to take on board.

The Heyday of the Industry in the 19th Century

An early reference by William Henry (1829) describes iodine manufacture (22):

> When all the soda has been separated by crystallization from a solution of kelp or barilla, or from the

> ley of ashes of marine plants, that afford the mineral alkali, the residuary liquor, in order to procure iodine from it, may be mixed with peroxide of manganese, and concentrated sulphuric acid be poured upon the mixture, in a retort furnished with a receiver. The iodine passes into the receiver, under the form of beautifiul violet vapours, which are condensed in crystalline plates, having the aspect of plumbago. To purify it from the redundant acid that comes over with it, the iodine may be re-distilled from water, containing a very small quantity of potassa, and afterwards dried by pressing it between folds of blotting paper. It is now manufactured largely for medicinal use, and may be purchased at a reasonable price.

At this time iodine could only be prepared from kelp liquor, not from barilla or other marine plants. Clearly by this date iodine was already available commercially, although demand was still low (23):

> Iodine was first manufactured in Glasgow, in 1818, by Dr. Ure of the Andersonian University. In 1824 to produce from 50 to 60 ounces per week was considered excellent working.

Thomas E. Thorpe writes in 1891 (24):

> In this country it was first made on a small scale by Dr. Ure of Glasgow, and the manufacture has since been almost exclusively confined to this city, where it has assumed considerable importance. It was first made there in quantity in 1841, and the imports of kelp in that year amounted to 2,565 tons. …now there are only two British works, both near Glasgow.

These references suggest that it had already been made in Glasgow for some years, having originally been imported from France, and most probably from the waste kelp liquors from soap boiling. These accounts refer to the time before the boom in iodine production in the mid-1840s, which led to a large number of small manufacturers getting involved. Ure appears to be one of the first people to make iodine in Scotland and to manufacture it on a small scale.

One of the early direct references to the industry in Glasgow, apart from that by Thomson above (15), is by Pereira in 1842 (25) where he says about iodine:

> That met with in this country was formerly imported. For many years however, it has now been manufactured in this kingdom. At the present time [1842], its British manufacture is, I believe, limited to Glasgow, where it is made from the kelp liquor in a leaden still, with which a series of spherical glass receivers is connected, and in which it is condensed.

It was also mentioned by Thomas Graham in the first edition of *his Elements of Chemistry* (1842), in which he briefly describes the extraction process and states (26):

> The greater part of the iodine of commerce is prepared at Glasgow from the kelp of the west coast of Ireland and the western islands of Scotland.

Mr. Whitelaw is mentioned by Pereira as a source of iodine in 1842 (27) and he was also mentioned in 1836 in an article by James Inglis on the electrical conductivity of iodine (28):

> The iodine I used was obtained from the manufactory of Mr. Whitelaw of Glasgow, where no iron vessel is ever employed, and which, in its veriest impurity, no iron can be detected.

Interestingly Sheridan Muspratt lists Whitelaw as a manufacturer in his *Chemistry Theoretical & Practical & Analytical* (29):

> Several manufacturers … may be found, among whom may be mentioned Mr. Whitelaw of Glasgow, and Mr. John Ward of the county Donegal, Ireland.

Despite Whitelaw apparently being well-known in Glasgow at this time, he does not appear in contemporary Glasgow directories and is not listed anywhere as either a soap maker or chemical manufacturer.

The 1840s appear to have been the boom years for the kelp to iodine industry in Glasgow (30):

> In the beginning of the year 1845, there were only four chemical manufactories engaged in the lixiviation of kelp, and manufacture of iodine, in and about Glasgow, and these not very extensive. During the following year these were increased to twenty establishments, several of which were very extensive indeed, and capable of working from 50 to 60 tons weekly. During this year the leys of the soap-boilers using kelp were eagerly sought after, and three of the above number of manufacturers were engaged in the extraction of iodine from soap leys solely, and other three parties partially occupied with this source. At present [1848] there are nine manufacturers in and about Glasgow engaged with the lixiviation of kelp, working up to about 85 tons weekly, (=4500 tons per annum). I estimate, however, that about 1500 tons of this quantity is consumed at Borrowstowness [(31)], leaving about 3000 tons for the Glasgow chemical manufacturers.

In 1856 we read in an American publication (32):

> Iodine is manufactured to a great extent by several houses in Glasgow; indeed, with the exception of one establishment in the N. of Ireland, a small one at Greenock, and another at Borrowstouness, all the British iodine is made in this city.

The names of most of these early manufacturers seem to have been lost to us. The lists of chemical manufacturers, for example in the annual Post Office Directory for Glasgow, do not usually indicate their products. Also the lists do not always seem to be complete, as some people known to be active are missing. Some firms or people, which are mentioned by name as producing iodine or processing kelp between 1840 and 1900, are shown below in Table 1, drawn from various sources, though this list is incomplete. It has been included to indicate the diversity and scale of the industry. There was a mini boom in the 1830s and then again in the 1840s, but from 1860 onwards only a few firms were involved. The ones in bold are the manufacturers about whom most is known in Scotland.

From the 1850s onwards there seems to have been only a handful of companies making iodine. For example, in 1866 we read a letter in *The Chemical News* by 'Kelp' listing manufacturers of iodine (33):

> Manufacture of Iodine.
>
> To the Editor of the Chemical News.
>
> Sir,—Like your correspondent, Mr. Paterson, I have been a subscriber to the Chemical News since the commencement of its publication. I have also observed the inquiry in reference to iodine in No. 364, and Mr. Paterson's reply in No. 365 ; but as he has omitted to give the names of any manufacturers except himself, I beg to subjoin the following, which, I believe, includes the names of all the iodine manufacturers in Great Britain:—William Paterson, Glasgow; John Ward and Co., Glasgow; The British Seaweed Company (Limited), Dalmuir, near Glasgow; John Carrol, Mile-end, Glasgow; F. R. Hughes and Co., Borrowstouness; John Loughran, Ramelton, Ireland; The Irish Marine Salt Company (Limited), Galway.
>
> I am, &c. Kelp.
>
> Glasgow, December 3.

By the start of the 20th century, it was down to four works in Scotland (34):

> The production of iodine from kelp, imported from the Hebrides, Ireland, and Norway, showed a marked decrease during the second half of the nineteenth century. In 1846 there were 20 factories in the West of Scotland; in 1900 the number had fallen to 4, which were situated at Falkirk, Clydebank, Kilwinning, and Bonnybridge. The fall in the value of potash salts, in consequence of the working of the deposits at Stanfurt [Stassfurt] in Germany, and the growing importation of Peruvian iodine were chiefly responsible for this decline.

The Size of the Iodine Industry in Scotland

It is clear from the companies listed above that the iodine industry was a substantial industry in Scotland for most of the second half of the 19th century. Charles Glassford gives details of the price of iodine in the 1840s, which went from a low of 12s. 0d. per lb. in January 1845

Table 1. Some Scottish manufacturers of iodine (all Glasgow or environs unless specified)

Irvine and Bryce	W. & M. Paterson
John Carrol	Montgomery Paterson
Cameron and Wood	Charles Penny
Hugh Donaghy	Thomas B. Porteous
Drygate Chemical Works	Port-Dundas Alkali Company
John Lang Dunn	William Readman
H.C. Fairlie (Falkirk)	William and Robert Rattray (Aberdeen)
Gilcomston Chemical Works, Aberdeen	Scottish Alkali and Acid Company, Kilwinning
Mr. Griffith	William Smith
Frederick Robert Hughes (Bo'ness)	**Edward C.C. Stanford** (whose companies traded under various names)
Innerarity, Dunn & Co.	John Ward (also in Ireland)
James Loughran (also in Ireland)	Andrew Ure
Milnquarter Chemical company, Bonnybridge	Ward and Smith (also in Ireland)
A. G. & D. Morton	William Watt
William Paterson	Mr. Whitelaw

to a high of 40s. per lb. in December 1845 (35). In 1846 prices fluctuated between 34s. 8d. and 16s. 0d. per lb., and by early 1848 had declined further to around 10s. a lb. The demand for iodine and the high price in 1845 caused an iodine boom and speculators moved in, and this explains the sudden increase in manufacturers and high price of iodine, which it was never to reach again. The amount of kelp coming into Glasgow increased with the demand, although it never reached the heights of the early 1800s, and Glassford records that (36):

> Numerous chemical manufacturers turned their attention to the business; persons were despatched to the shores of Ireland and our Scottish isles, to increase the quantity of kelp made, to buy it up at low prices; and for a time much excitement prevailed.

Table 2 shows the kelp imports into Broomielaw on the Clyde for Glasgow from 1841 to 1847. Glassford estimates that in 1845-46, the boom year, total imports reached 10,000 tons, as 3,000 tons were being processed at Bo'ness on the Forth, and a further 900 tons were also landed at other ports on the Clyde. This was still only about half the amount used at the height of the kelp boom. By 1848 only about 600 tons of kelp were being used in soap-making in Glasgow and the majority was now used for the extraction of iodine and potassium salts. In 1845 John Ward, almost certainly from Glasgow, opened an iodine factory in Ramelton, County Donegal, the first such in Ireland. Glassford records that a manufacturer consumed 700 tons of kelp on Irish shores in the first nine months, presumably this was Ward. J. Ward, and also in London as Ward and Smith, are both listed as manufacturers of iodine in Glasgow, and presumably the Irish company was set up by them. In 1862 Messrs J. Ward & Co. of Glasgow exhibited at the International Exhibition in London, the only Scottish manufacturer to do so, although three French manufacturers also exhibited products from kelp. Ward exhibited iodide of potassium, chloride of potassium and sulphate of soda (37).

Table 2. Kelp imports into Glasgow (from Glassford (36))

Period July-July	**Amount/tons***
1841-1842	2,565
1842-1843	1,887
1843-1844	1,965
1844-1845	3,263
1845-1846	6,086
1846-1847	3,627

*1 ton = 2,240 lb = 1.018 metric tonne

Irish kelp was more valuable than Scottish kelp due to its higher iodine content and was worth up to £10 a ton, often double the value of the Scottish kelp. This explains why Irish kelp was so important to the Glasgow iodine industry in the 19th century. The reason why Irish kelp was richer in iodine was mainly because they used deep-sea drift weed, blown ashore in the winter, or harvested at low tide offshore in the spring, whereas in Scotland they traditionally used intertidal cut weed, consisting of different seaweed varieties, which were poorer in iodine. Not all seaweeds are equal when it comes to iodine or potash content, and the rods (stems) are richer than the fronds. The art of making good kelp was to harvest the right seaweeds at the right time and to store them properly, away from rain, avoid contamination with sand, and burn at a low temperature to an ash rather than a slag.

Stanford extends this data up until 1875 in his 1884 article, as shown in Table 3, covering the period in blocks of 5 to 10 years. From this we can see that the iodine industry continued to develop from 1845 onwards and was still healthy in 1875, with an average consumption of 9,187 tons of kelp in the previous ten years. The price of iodine had also held up, and although there were still speculative highs, the average in the last ten years 1866-1875 was a respectable 15s. 11½d. per lb., the highest average since 1846-55. This is equivalent to about £1,700 per ton, showing how valuable iodine had become. (This would be worth £215,609 per ton in 2022.)

Table 3. Kelp production and price of iodine (from Stanford 1884 (38))

Years	Tons of kelp		Price of iodine per lb.	
	Average	Range	Average	Range
1841-45	3,133	1,887-6,086	11s. 9d	4s. 8d.-31s. 1d.
1846-55	5,811	3,267-11,421	12s. 11d.	8s. 8d.-21s. 3d.
1856-65	9,730	6,349-14,018	8s. 10d.	5s. 0d.-13s. 8d.
1866-75	9,187	8,116-10,923	15s. 11½d.	10s. 0d.-34s. 0d.

The amount of kelp processed rose steadily over this period from a low of 1,886 to a high of 14,018 tons per year. The price of iodine also varied widely from a low of 4s. 8d. to a high of 34s. 0d., and on average its price increased over this period. This was because of the expanded market for iodine as more uses were found for it. In 1874 the first shipment of South American iodine arrived in Europe, although it had been discovered in caliche some years earlier (39). This was the first threat to

the monopoly of kelp for iodine production since its discovery, undercutting the Scottish price by 15%. In 1884 E. C. C. Stanford could state authoritatively, "The present price [of iodine] is 5s. [per lb.] at which its production from ordinary kelp is uneconomic" (40). The price had thus dropped dramatically in the ten years or so since Chilean iodine had become commercially available in Europe. This led in the late 1870s to the setting up of an iodine syndicate (also known as a combination or cartel) between South American and European producers, which initially fixed the iodine price at 10 ½ d. per oz (14 s. per lb). This stabilized the industry and allowed the Scottish and French producers to continue despite the competition from Chilean iodine. This syndicate lasted, on and off, from the 1870s until the 1930s, reputedly the longest of any of the 19th century cartels (41).

The iodine from kelp manufacturers were known as lixiviators, since the key step was the extraction of soluble salts from the kelp slag or ash by lixiviation, i.e., extraction of salts from a solid using a solvent, usually water. In the Stanford papers in the Mitchell Library, Glasgow, Stanford gives a list of Scottish lixiviators in 1861, just before he entered the market in 1863 (Table 4).

Table 4. List of lixiviators of kelp in 1861 in Glasgow and their annual production in tons (42)

Hugh Donaghy	300-350
John Loughran	300-350
Mr. Readman	700-800
Mr. Griffith	300-350
Montgomery Paterson	1000-1500
William Paterson	7500-8000
(Totals:	**10,100-11,350)**

John Loughran is also mentioned as running the Rathmelton Iodine Works in Ireland in 1864. In 1864 William Paterson was reputed to be the largest iodine manufacturer in the world and he was the dominant manufacturer in 1861 in Glasgow (see Table 4), at which time he processed 80% of Glasgow's kelp and hence presumably 80% of the iodine produced. He is discussed further below. Note also Montgomery Paterson, who was William's son, and they are later recorded together as Wm. & M. Paterson, chemical manufacturers. This company and Wm. Paterson are recorded as existing at the same time and at the same location, at the Whitevale Works, Camlachie, Glasgow.

A letter from William Paterson in November 1866 lists the iodine production from four works then extant, in reply to an earlier request to know who manufactured iodine in Glasgow (43). Paterson lists four works, which produce 90% of all the iodine produced.

Works #1	20 kegs
Works #2	100 kegs
Works #3	150 kegs
Works #4	1000 kegs

The last works was identified as Paterson's and this makes a total production of 1,270 kegs. Iodine was usually shipped in small wooden barrels known as kegs, containing 1 cwt or 112 lb. of iodine. This production thus amounts to 142,240 lb. or 63.5 tons of iodine. At 10s. per lb. in 1866 this iodine would be worth £71,120. In 1866 "Kelp" had listed iodine manufacturers in Great Britain, in reply to the earlier letter by Paterson, referred to above, and identifies William Paterson, Glasgow; John Ward and Co., Glasgow; The British Seaweed Company (Limited), Dalmuir, near Glasgow; John Carrol, Mileend, Glasgow (33). "Kelp" is obviously well informed about the current situation in Glasgow, more so than the textbooks of the time. Five manufacturers are listed in Scotland, and one of these works is in Bo'ness, which is on the Firth of Forth, in the east of Scotland, and not in Glasgow. Paterson only refers to the four works located in Glasgow. The Bo'ness works were owned by Frederick Robert Hughes (1803-1895) and continued in operation until the1880s.

In 1872 we find in *Wagner's Handbook of Chemical Technology*, "The chief seat of iodine manufacture is at Glasgow, where there are twelve factories; there are two iodine factories in Ireland and two at Brest, in France." And later in the book, "The process of Stanford is carried out on a large scale by the British Sea-weed Company, at Dalmuir, near Glasgow." The figure of 12 works in Scotland appears to be out of date and in Ireland at this date there were two works in Ramelton (Donegal) and Galway city. Wagner states that in 1869 1,829 cwt. (91.45 tons) of iodine were produced in Scotland and Ireland, out of a global total of 3,453 cwt. (172.65 tons), and 300 cwt. (15 tons) of bromine were made in Scotland. They go on to say (44):

> In Paterson's large iodine works at Glasgow this operation is carried out in a cast-iron hemispherical vessel of 1.3 metres diameter, the cover being a leaden dome, to which are fitted two earthenware stillheads, connected by means of porcelain tubing with two earthenware receivers, each consisting of 4 or 5 parts.

Initially glass vessels were used to collect the iodine as in Figure 4, later replaced by earthenware udells. There might be several lines of condensers running off a series of iodine stills in a large works (Figure 6).

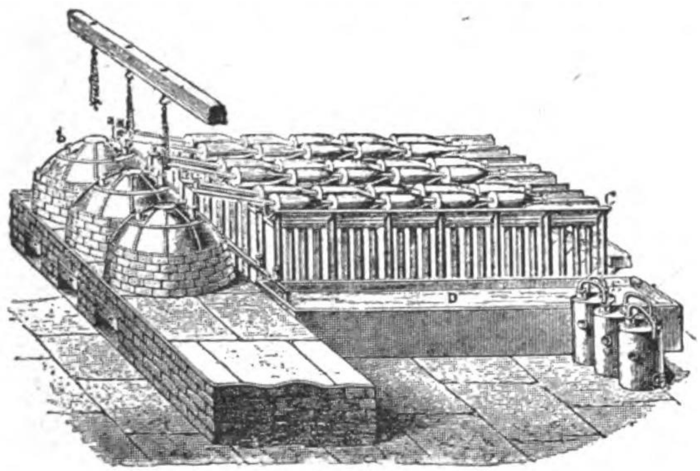

Figure 6*. Iodine stills showing earthenware udells, indicating the scale of the developed industry (45).*

Thomas Newstead (1842-1910) is listed in the Glasgow City Archives as having been a chemist at Whitevale Chemical Works from 1874-1892, i.e., from just after the death of William Paterson. The works is described thus (46):

> The chemical works of William Paterson (c 1786-1873) produced iodine, chloride of potassium, sulphate of potash and other chemicals from kelp and was described as the largest of its kind in Europe, or the world, in 1864 (Weekly Mail, 30 Jan 1864).

Economics of the Kelp Industry

After 1841 iodine was the main product obtained from kelp, but not the only one, and it would not have been economic to extract only iodine from kelp, at around 10-15 lb. per ton of kelp, especially with its fluctuating price. In fact, the other chemicals obtained from kelp helped to make the whole process viable. Hardly anything was wasted and even the kelp waste was sold off as a cheap manure.

An example of the promotion of kelp waste by John Ward is given below (47). Other Glasgow manufacturers did the same and John Ward also published similar adverts in Ireland for waste from the Ramelton works. The key to a profitable enterprise was to waste nothing.

> WASTE IODINE MANURE.
>
> The waste iodine or kelp liquor of the iodine makers has lately been applied by Mr. John Ward, of Glasgow, to the manufacture of manure. The waste iodine or kelp liquor, instead of being thrown aside as valueless, according to the system hitherto pursued by the manufacturing chemist, is, according to the present improvement, utilised and turned to valuable account, by being discharged into a proper receiver, where unslacked lime is added to and mingled with it. This produces a powerful fertiliser, which may be judiciously used by the farmer in combination with other substances of various kinds, just as will best suit the circumstances under which the manures are to be employed on the land.

Thomas Porteous, who had previously made iodine in Glasgow, gives an interesting snapshot of the iodine industry in 1854 in an American publication, and he quotes prices in dollars (48). He worked on the basis of an annual use of 9,000 tons of kelp, between Scotland and Ireland, and uses an average of 9 lb. iodine/ton of kelp. He discusses the industries in Scotland, Ireland and France; the latter he judges to be considerably smaller than that in Scotland and Ireland at the time.

Porteous estimates that 9,000 ton of kelp would produce:

81,000 lb. iodine at 9 lb. per ton

4,500,000 lb. potash at 500 lb. per ton

1,250,000 lb. sulphate of potash at 150 lb. per ton

2,700,000 lb. mixed carbonate, muriate (chloride) and sulphate of soda (kelp salt) at 300 lb. per ton.

All of these had some value, including the solid kelp waste, which was sold to Glasgow glass makers, who mixed it with sand and used it as a flux. Porteous uses current values to estimate the value of these products to Scotland and Ireland (Table 5). Iodine was worth 63% of the saleable products and thus even when potash from Stassfurt reduced the price of potash, it was still possible for iodine manufacturers to continue operating.

Table 5. Products of the iodine industry in Scotland and Ireland (48)

Iodine:	
81,000 lb. at $3.00 per lbs:	$243,000 (63.3%)
Chloride and sulphate of potash:	
2,600 tons at $50 per ton:	$130,000 (33.9%)
Soda salts:	
1,350 tons at $5 per ton:	$6,750 (1.76%)
Kelp waste:	
4,000 tons at $1 per ton:	$4,000 (2.04%)
Total value:	**$383,750**

The production of iodine estimated here amounts to 36.2 tons, and the Scottish industry seems to have produced typically 40-60 tons iodine per year. Porteous goes on to give a detailed description of the process for producing iodine from seaweed. Interestingly, the USA did not produce its own iodine until the early 20th century, when in World War I it turned to Californian seaweed to produce potash and iodine, and also acetone. Variations in the value of iodine had a major effect on profitability, and when the Stassfurt potash deposits started producing in the 1860s, the value of the potassium salts almost disappeared (49).

By 1877 the number of Scottish manufacturers had dropped to just three: W. & M. Paterson; Mr. Hughes (Bo'ness), and the North British Chemical Co. (E. C. C. Stanford), although in 1878 H. C. Fairlie started extracting iodine in Camelon, near Falkirk, in the East of Scotland and continued into the 20th century, finally being liquidated in 1954. In 1901 the British Association Handbook on the Industries of Glasgow and the West of Scotland records four firms (50), but Paterson's and Hughes had both closed in the 1880s.

> At the present time the extraction of iodine from kelp is prosecuted by Mr. H. C. Fairlie at the Camelon Chemical Works, Falkirk; by the British Chemical Co., at the Whitecrook Works, Clydebank; by the Scottish Acid and Alkali Co., at the Longford Chemical Works, Kilwinning; and by the Milnquarter Chemical Co., Bonnybridge.

The works of H. C. Fairlie in Camelon, Falkirk, were located on a canal, like Stanford's Whitecrook Works in Clydebank, allowing for easy shipment of raw materials and products, and Hughes' iodine works in Bo'ness were near the docks. Sea access and good communication were important as the raw material (kelp) was bulky and was imported by sea from Ireland or the Scotland islands, where it was made.

The Prominence of William Paterson (1786-1873)

One name that crops up again and again in the history of the extraction of iodine in Glasgow is that of William Paterson (variously spelled Patterson and Pattinson). He is frequently cited as the dominant manufacturer of iodine in Glasgow, processing around 80% of the imported kelp in the 1860s. W. Paterson was still listed in business in 1877, after his death, but the company appears to have gone out of business in the 1880s. William Paterson had dominated the Glasgow iodine industry for at least 30 years.

He was born in Gifford, Haddingtonshire, and died at the age of 87. His obituary appears in Stanford's papers but does not appear to have been written by Stanford, as the author says he says he knew Paterson for 25 years and Stanford only moved to Scotland in 1863/4 and Paterson's dates are 1786-1873 (51).

> By-and-by he [Paterson] settled in Glasgow as a wine merchant. Not succeeding, however, as he would have desired, he renounced the wine trade after several year's experience, and having in addition to his ample general knowledge, a good understanding of the science of chemistry, he commenced the manufacture of iodine and other products from kelp. In this useful branch of chemistry he was entirely successful, owing, no doubt, not only to the thorough knowledge of what he had undertaken, but to his untiring application to the business in all its scientific and mercantile details. During the time we knew Mr. Paterson—fully a quarter of a century—he never left Glasgow either for the coast or the country."

In 1850 Paterson wrote in a letter (52): "I have been intimately and extensively engaged in the consumption of kelp, for various purposes, since the year 1815." He seems to have been in business as an iodine manufacturer from around 1842 to his death in 1873, and was in partnership with his son Montgomery Paterson. At one time there were two separate companies listed, W. and M. Paterson and Wm. Paterson, as chemical manufacturers and producing iodine, at the same location at the Whitevale Chemical Works, Camlachie.

In 1882 an article by J. W. Cochrane describes iodine manufacture from kelp at Messrs. Paterson's works and quotes them as processing 8,000 to 10,000 tons of kelp each year, producing 2,400 tons of potassium chloride, 500 tons of potassium sulphate, 40-50 tons of iodine and 5 tons of bromine (53).

We have an account of Paterson's works in 1876 in the BAAS report, and the high usage of coal as a fuel is interesting (54):

> Kelp, obtained from sea-weed, collected and burned in the Western Highlands and in Ireland, had long been used in Glasgow for soap-making, the aqueous extract being causticized with lime and the alkaline lye boiled with the fat. In the works of Messrs W. & M. Paterson, the great makers of iodine, the process pursued is shortly as follows:- The kelp is lixiviated with water in large vats, and the liquor is boiled down to required strengths, by which the muriate and sulphate of potash and "alkaline salt" are separated by alternate precipitation and crystallization. The remaining mother liquor, which has a density of 1.5,

> contains the soluble iodides, bromides, sulphides and hyposulphites. By adding sulphuric acid the two latter are decomposed, and sulphur is precipitated, which can be collected, and the clear liquor is treated with excess of sulphuric acid and manganese in retorts, when the iodine distils over and is collected in earthenware receivers. The bromine is subsequently separated by further addition of manganese [presumably he means manganese dioxide], and collected in suitable condensers. The iodine is purified by sublimation if necessary. The iodine and bromine are converted respectively into iodide and bromide of potassium—the two compounds chiefly used—by dissolving in potash, igniting gently to decompose the iodate and bromate which are formed, and crystallizing the salts. These compounds are made by Messrs. Paterson. This firm uses from 8,000 to 10,000 tons of kelp annually, which yield about 2,400 tons of muriate of potash, 500 tons sulphate of potash, 45 to 50 tons of iodine, and 5 tons of bromine. About 8,000 tons of coal are consumed in the works.

In an article in 1889, on the Glasgow Exhibition, Professor Dittmar discusses the state of the iodine industry in Glasgow, and states that due to the importation of cheap iodine from Peru, the Scottish iodine from kelp industry has become unviable. "As a consequence, the famous iodine works of Messrs. Paterson and Co. were closed" (55). This is the last we hear of William Paterson's iodine works.

Edward C.C. Stanford (1836-1899)

Edward Stanford took on the mantle of William Paterson as Scotland's pre-eminent iodine manufacturer from the 1880s (56):.

> Mr. Stanford's name is intimately associated with the British iodine and kelp industry, the seat of which has always been Glasgow. This illustrates generally the manufacture of iodine, bromine and potassium salts from seaweed, besides that of the new and interesting substance Algin, first isolated and studied by Mr. Stanford.

Looking back at the 19th century iodine from seaweed industry, Edward Stanford stands out as the leading figure in research and development, as well as in manufacture. He worked indefatigably from 1863 until his early death in 1899 to make the seaweed and kelp industry more profitable, particularly for the Scottish kelpers he first met in 1863 on Tiree, a windswept island off the west coast of Scotland. He developed the char process to improve iodine yields, although it was not a success in the long-term. In his prize-winning paper in 1862 on this new process for obtaining iodine from seaweed, based on work done in his father's laboratory in Worthing, he stated his philosophy and reason for doing the work (57):

> I think I may be permitted to say that the present is about the worst method that could be adopted; for the poor kelper innocently throws away in the white smoke of his vraic [(58)] fire substances which thus dissipated prove an intolerable nuisance, and banish him as an exile from civilisation, but which collected, would keep him from rags and starvation, dangers which too often at present threaten him.

As well as the works at Clydebank, where his was the first factory to be set up, Stanford also had works in Tiree and N. Uist in the Hebrides, and at Freagh, County Clare, Ireland, though the latter was only operating for a couple of years. His first factory at Tiree was in operation from 1863 to 1901. He was always trying to improve the extraction process and make the industry more profitable, and in the 1880s, using a cold, wet extraction method to save fuel, he discovered alginic acid, which he called algin. Long after seaweed ceased to be an economic source of inorganic chemicals, alginic acid was to become the savior of seaweed industry from the 1930s onwards, and still continues to this day in Ireland and Scotland. Stanford's interesting story as a chemical entrepreneur will be covered in a later article.

Stanford's British Chemical Co. was the successor to the North British Chemical Co., which in turn was the successor to the British Seaweed Co. It was run by E. C. C. Stanford until his death in 1899. There was also a firm called Stanford & Co. Ltd. (in 1936), located in Stanford Street, Clydebank, and existing at the same time as the North British Chemical Co., which also made alkali (59).

> The works were erected over a century ago for the purpose of extracting iodine, bromine, and potash salts from seaweed charcoal, a substance which was the discovery of Commissioner E. C. C. Stanford, and the manufacture took place in Tiree, North Uist in the Hebrides, and in County Clare, Ireland. The first and most important of these works was erected in 1863, in the Island of Tiree, and the whole process was at first carried there. Owing to the difficulty of importing fuel, however, it was deemed advisable to remove the extract works to Clydeside. Iodine, bromine, muriate and sulphate of potash and kelp salts were at first the only manufactures, but the works gradually extended to make iodide of potassium for the same purpose, carbonate of potash or pearlash, oil of vitriol, muriatic acid, salt cake, caustic soda, chlorate of potash, bleaching powder etc. The works, which stand on about ten acres of ground, of which the company—the North British Chemical Company

> Limited—farmed upwards of a hundred acres, were subsequently demolished for reconstruction; and for many years afterwards Mr. Stanford's inventive genius produced there some of the finest chemical products in the world.

The Challenge from Chile and the Decline of an Industry

1874 was another of the black years for the kelp industry, with its overtone of the introduction of synthetic soda in 1823 and later the importation of cheap potash from Stassfurt in the 1860s. Three-quarters of the way through the 19th century, the first commercial export of crude iodine, a by-product of the South American nitrate deposits, arrived in Europe in the 1870s. Both the nitrate deposits in Chile and the potash deposits in Germany are finite resources, but seaweed is an essentially infinite and renewable resource. Chile is still the world's largest producer of iodine from the caliche deposits. The price of iodine dropped, as Stanford had recorded in 1884, because the Chilean industry could produce ten times the amount of the current annual market demand for iodine and more cheaply than its production from kelp. Iodine as sodium iodate is present in small amounts in the Chilean nitrate deposits, and after extraction of the iodine by reduction (not oxidation as in the case of kelp), it was distilled and purified in a similar way. It is amazing looking back that the Glasgow iodine industry could survive until the 1930s in the face of such competition. The market share of kelp iodine declined steadily, but it survived due to the iodine syndicate, between the European and Chilean iodine producers set up in 1878. This cartel lasted for over 60 years, and maintained stability in the industry until it collapsed in the 1930s. It was in all their interests to keep the price of iodine up, and not flood the market, and the last Glasgow and Irish factories only closed when this agreement was terminated. The French continued to make iodine from seaweed into the 1950s and small amounts are still made in Japan.

W. G. O'Beirne, Managing Director of one of the last Glasgow iodine factories, which was Stanford's old firm, said in 1916 that his firm (42)

> had spent £40,000 on research and on the creation of a factory for the distillation of seaweed, had lost all their money and had obtained nothing but an evil-smelling tarry water of no use for anything.

Ernest Booth contradicts this statement on the profitability of Stanford's company in his chapter on seaweed in *Chemical Oceanography* (60) and in his article on Stanford (61). However, it may also be true that the company lost money on the Tiree factory and others the company set up on the Scottish islands, but made money in other ways. The industry struggled into the 20th century.

The most extensive written account of the Glasgow iodine industry is in the book on local industries produced for the 1901 British Association meeting in Glasgow by George G. Henderson, and it is of interest as the fullest description of the twilight of the iodine industry in Scotland at the start of the 20th century (62).

> The extraction of iodine from kelp is an industry which has been prosecuted in the West of Scotland for a long time. Iodine was first made in quantity in Glasgow in 1841; in 1846 there were twenty makers, and now there are only four. The chief reasons for the closing of so many works were the fall in the value of potash salts, as a result of the exploitation of the great mineral deposits at Stassfurt, the great fluctuations in the price of iodine, and, last, but not least, the importation of iodine obtained from caliche, the crude nitrate of soda found in Peru, which now forms the most important source of iodine. Iodine from caliche was first sent over to this country in quantity in 1874, and since then the import has steadily increased. The present output from this source must be five or six times the total production of Europe.
>
> In the West of Scotland iodine is extracted from kelp, a rough slag obtained by burning seaweed in long narrow pits, or charring it in retorts. Kelp comes from the Hebrides, from Ireland. and from Norway. The average annual imports into the Clyde were, for the ten years prior to 1876, 9187 tons; for 1876-1885, 6887 tons; and for 1891-1900, 6841 tons; the quantity imported has been practically stationary since 1876. Kelp was formerly used as a source of sodium carbonate, but now it is only used for the extraction of potassium salts—the sulphate and chloride, which are used principally for manurial purposes—and of iodine, which is either sold as such, in cakes or resublimed, or made into iodides of sodium and potassium, or into iodoform, the only additional new product of recent years. In making kelp for iodine only those kinds of seaweed which are always submerged are used; these are torn up by the storms of winter and cast ashore. If the seaweed is properly burned to a loose ash at a low temperature it ought to yield about 25 lbs. of iodine per ton of kelp, but, as it is difficult to avoid too high a temperature in the ordinary process of kelp burning, average kelp does not contain more than 12 lbs. of iodine per ton.
>
> The process employed for the extraction of the iodine remains practically the same as it was. The kelp is broken up and lixiviated with hot water in vats heated by steam, and the clear solution is run off and boiled

> down in hemispherical iron pans. The salts which separate are fished out, the liquid is cooled, and another crop of crystals is removed; the process of boiling down, cooling, and removal of the crystallised salts is continued until the mother liquor has become sufficiently rich in iodine. The salts removed by crystallisation are chiefly potassium sulphate, potassium chloride, and "kelp salt," a mixture of the chloride and carbonate of sodium. The mother liquor is mixed with about one-seventh of its volume of sulphuric acid, when the sulphides, sulphites, and thiosulphates present are decomposed and a considerable quantity of sulphur is deposited. The mother liquor is strained off from the sulphur, and run into the iodine still, a deep iron pot covered with a strong leaden lid, to which are luted two earthenware arms, which are connected with two series of peculiarly shaped stoneware condensers, called udells. The still is heated, manganese dioxide is added at intervals, and the iodine, which is carried over with the steam, is condensed in the udells, which are not changed until they are full. The iodine is purified by resublimation in small covered pans of earthenware or porcelain.
>
> At the present time the extraction of iodine from kelp is prosecuted by Mr. H. C. Fairlie at the Camelon Chemical Works, Falkirk; by the British Chemical Co., at the Whitecrook Works, Clydebank; by the Scottish Acid and Alkali Co., at the Longford Chemical Works, Kilwinning; and by the Milnquarter Chemical Co., Bonnybridge.

According to Clow and Clow (63) the 1914-18 war revived the kelp industry temporarily to produce potash and iodine. They list

> The purchasers of the kelp [as] (1) The British Chemical Company Limited, Whitecrook Chemical Works, Clydebank; (2) Messrs. H.C. Fairlie and Company Limited, Camelon Chemical Works, Falkirk; (3) Scottish Alkali and Acid Company, Longford Chemical Works, Kilwinning; (4) Milnquarter Chemical Company, Bonnybridge.

I can find no earlier mention of kelp to iodine factories at Kilwinning or Bonnybridge (which is next to Camlachie).

The industry staggered on and in 1928 a US survey of the iodine industry said this (41).

> The iodine consumed in the United Kingdom is supplied chiefly by imports, although there is a small production from kelp and tangle ash. At one time considerable quantities of kelp were gathered on the Irish coast and shipped to Scotland for extraction, but it is understood that, owing chiefly to increased labor costs the Irish industry is now practically non-existent, and any seaweed gathered is employed as fertilizer on land near the coast.

The same source names three firms still extracting iodine from kelp: British Chemical Co. (Ltd), Clydebank, Scotland, H. C. Fairlie & Co. Ltd, Falkirk, Scotland, and Stevens & Sons, Sheppey, England, the first two being the main manufacturers located in Scotland. It states that the small production from kelp in Scotland includes ash imported from Norway. The report quotes sources for Scottish production figures for 1916 to 1927, with a high of 45 and a low of 18 tons per year, and an average of 31.6 tons per year. It states there was a rise in production from 1906, and in 1913 1,144 tons of kelp slag and tangle ash was produced. Kelp slag contains less iodine than the loose tangle ash. The industry was not dead but it was clearly dying and only World War I produced a short-lived revival.

Conclusions

I was amazed to find that there was little written about the Glasgow iodine industry, considering its importance to the local economy as well as to the survival of the kelp industry in Scotland and Ireland. Most information is available about Edward Stanford and his ventures in Scotland and Ireland, and his company remained a player in the kelp to iodine industry until its demise in the 1930s. The biggest company, that of William Paterson at the Whitevale Works, Camlachie, Glasgow, seems to have virtually disappeared from history. At one time he processed around 80% of the kelp imported into Glasgow, and was the major player in buying up Irish kelp through his agents. In 1864 his Whitevale Chemical Works processed 11,300 tons of kelp per year (64). I have not come across any photographs of the various Scottish iodine works, although there is a wealth of paintings from the 19th century and photographs from the early 20th century of kelp burning and seaweed collection. Stanford was known to be a keen amateur photographer in his youth in Worthing, England, and it is surprising that he did not keep a photographic record of his endeavours, although it may be that some are in existence.

By the late 1880s the iodine industry was struggling in the face of the competition from South America and potash and bromine from Germany, but Stanford's company and a few others survived into the 20th century (65). This important chemical industry in Glasgow and the lowlands of Scotland was overshadowed by larger concerns, especially the St. Rollox works of Charles Tennant and Charles Mackintosh, and the other enterprises of

Charles Mackintosh (66). Given the status of iodine as a valuable commodity in the mid-19th century, in medicine and photography and the dye industry, in which many people speculated and fortunes were made and lost, I am surprised it has not been researched properly or been given a full treatment. Due to the paucity of sources, this article is only a provisional and introductory treatment, and I was interested to see a Ph.D. studentship advertised in Glasgow in 2021 on this topic (67).

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This research project will transform our understanding of the role of industrial seaweed exploitation in early modern Scotland, by focusing on its technology and social impact, and the human experience of those involved. Drawing on archaeological and documentary sources, it will also consider its historical context and examine, for the first time, the rich seam of evidence in Gaelic and Scots about the commercial exploitation of seaweed and its impact on communities across Scotland.

About the Author

Dr. Peter Childs taught Chemistry at university level from 1970 until retiring in 2009, at Makerere University, Kampala, Uganda (1970-76) and later at the University of Limerick, Limerick, Ireland (1978-2009). He became interested in the early Irish chemical industry and has been researching this for the past 20 years. He has worked extensively with Irish chemistry teachers—producing *Chemistry in Action!* magazine since 1980, starting the annual ChemEd-Ireland conferences, and running in-service courses and workshops. He is a past President of the Irish Science Teachers' Association and also of the Institute of Chemistry in Ireland. He is still active in chemical education, nationally and internationally, and is a past chair of the EuCheMS Division of Chemical Education (2002-2008). He has supervised a number of Ph.D. and Masters students in chemical education and been involved since 2010 in three EU-funded science education projects (SALiS, TEMI and ARTIST). He was a member of the first EuChemS Historical Landmarks Selection Committee (HLAC), 2017-2021. He has just published a series of articles on the local kelp industry in Ireland in Galway, County Clare and County Donegal, all major centers.

Partington Prize 2023 Open for Submissions

The call for submissions for the 2023 Partington Prize is now open. The Prize is awarded every three years for an original and unpublished essay on any aspect of the history of alchemy or chemistry. The competition is open to anyone with a scholarly interest in the history of alchemy or chemistry who, by the closing date of 31 December 2022, has not reached thirty-five years of age, or if older is currently enrolled in a degree program or has been awarded a master's degree or Ph.D. within the previous three years.

The Society for the History of Alchemy and Chemistry established the Partington Prize in memory of James Riddick Partington, the Society's first Chairman. The prize consists of five hundred pounds (£500) if awarded to a single essay.

The deadline for entries is 31 December 2022. Details on entering appear in the May 2022 issue of *Ambix* and can be found at https://www.tandfonline.com/doi/full/10.1080/00026980.2022.2054608

A PIONEER IN CHEMICAL LITERATURE: LIBRARIAN MARION E. SPARKS

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Introduction

Marion Emeline Sparks (1872-1929) was the University of Illinois at Urbana-Champaign's (UIUC) first chemistry librarian in the early 20th century. During her tenure as librarian, she taught classes in chemical literature, published papers and books on chemical information, conducted bibliographic research, translated foreign language publications in chemistry, and became a trusted colleague of chemistry library patrons. In 1919, she self-published *Chemical Literature and Its Use*, the first chemical information textbook of its kind, with a widely distributed second edition published in 1921 (1). Sparks established the importance of the Chemistry Library at UIUC and trained Illinois chemists to appreciate and contribute to the literature of the chemical sciences.

Figure 1*. Marion Sparks in the Chemistry Library (History of Chemistry Library collection, University of Illinois Chemistry Library. No information on creator or reproduction rights found with the image, 2022.)*

This article is dedicated to furthering knowledge of Miss Sparks' life and teachings. Between attending the University of Illinois as a student and her employment there, she spent nearly forty years on campus. A plaque hangs in her memory in the UIUC Chemistry Library, and her influence on the chemistry library continues through the Marion Sparks Award for Professional Development awarded by the Special Libraries Association Division of Chemistry (2).

Early Life and Academics

Marion Emeline Sparks (Figure 1) was born on December 5, 1872, on a farm in Miller Township (LaSalle County), Illinois. Her parents, George and Esther Peacock (Clifton) Sparks, both taught in elementary country schools. She had a sister, Annie Elnora, six years her junior.

Sparks attended both Seneca and Marseilles (Illinois) High Schools before graduating from Ottawa Township High School in 1892 where she received the LaSalle County University of Illinois-Honorary Scholarship. At the time, each Illinois county promulgated that

county residents, 15 years of age or older, were eligible to take a two-day examination and the student with the highest score, male or female, would receive a full scholarship to the University of Illinois. Sparks achieved the highest score in LaSalle County's honorary scholarship for full tuition to the University of Illinois in Urbana.

Sparks began her Bachelor of Arts (BA) in Classics in the fall of 1892, earning that degree in June 1895. She was one of nine female students in a campus-wide class of 73 graduates. As part of the requirements for the completion of her degree, Sparks wrote a thesis, entitled, *History and Functions of the Areopagitic Senate*.

In 1896-1897, Sparks began work on her master's degree in Classics, before putting this coursework aside to study library science. She took classes in the School of Library Science from 1897-1899, earning her Bachelor of Library Science in June 1899. *Founding a Public Library in Illinois* was the title of her second thesis.

In 1899, Sparks resumed her courses for her master's degree. earning her Master of Arts (MA) degree in Classics in June 1900. The title of her master's thesis was *The Forms of Address in the Athenian Orators*.

During her time as a student on campus, Sparks participated in several activities and held assorted leadership positions. Marion was a member of the Young Women's Christian Association (YWCA) and served in several leadership roles between 1893 and 1895. Sparks was also part of Alethenai, a literary society for women, and served a term as president in 1895. Between 1890 and 1893, she participated in Christian Endeavor, Library Club, and the Watcheka League. Each year between 1894 and 1900 she contributed to the *Illio Yearbook.*

Throughout her education, Sparks' early coursework played a role in the services she eventually provided to her chemistry library patrons. While earning her BA degree, she studied French, German, Greek, Italian, Latin and Spanish. Sparks later applied this training by translating foreign language chemistry articles.

Early Career

Ms. Sparks' first library-related work experience began in 1894, when she worked as a student assistant at the Loan Desk in the University of Illinois Main Library. She held this position until 1897.

From 1898-1904, Sparks began a series of several positions organizing library collections across the Midwest United States. While finishing her Master's degree she began to help catalog the collection of the Urbana Free Library. Miss Sparks spent 1900 at the Davenport (Iowa) Academy of Science. From January-June, she contributed to the institution's foreign correspondence; from June to December, she organized their library. After a brief hiatus, from October 1902-February 1903, she organized the Elkhart (Indiana) Public Library. For the two subsequent months, she selected children's books for the library. Sparks then spent June to November organizing the collection of the Kansas City (Kansas) Public Library. Her last job of this sort, at Dowagiac (Michigan) Public Library, ran from January to March 1904.

In 1904, Sparks returned to Urbana, and was employed as a resident bibliographer in the Nutrition Investigation Laboratory until 1910. She also volunteered her evenings from June to August 1905 again helping the Urbana Free Library implement their new charging system.

Overcoming Barriers

As is the practice today, references for new librarians were often required from their former faculty and instructors. Katherine Lucinda Sharp, Head of the University Library and first Director of the new Illinois Library School, provided Marion with several letters of reference. Sharp was a former student of Melvil Dewey, the creator of the Dewey Decimal Library Classification schema and co-founder of the American Library Association. Katherine Sharp was responsible for the development of the library collection at Illinois and pushed for more stringent standards for library services and admission requirements to the library school. Although not considered professional qualities at the time (3, 4), Katherine Sharp criticized Marion's attractiveness, personality, and manner of dress to various prospective employers in the early 1900s. An example is a 1902 letter to H. H. Ring of Houston, Texas:

> Dear Mrs. Ring:
>
> In answer to your questions concerning applicants for the position of cataloger in your library, I can only honestly say that I can not [*sic*] favorably recommend Miss Mary [*sic*] E. Sparks. She does not possess tact in any marked degree, and personally she is very unattractive. She is probably a woman of great ability as a scholar, but beyond this I can give not [*sic*] favorable recommendation for her.
>
> Miss Arnold of whom you speak is a very attractive young woman, and her work while in the library school was of good average quality. I think that you would make no mistake in engaging Miss Arnold to

> assist you. She would surely be very attractive to the public and you could trust her work.
>
> Yours very sincerely,
>
> Katharine L. Sharp [signed]
>
> Director of Lib. School

Another statement sent to Mr. Windsor for the Fisk Agency in August 1910 reads:

> Miss Marion Sparks completed the Library School course in the U. of I. several years ago, and since that time has held many temporary positions as library organizer and as bibliographical expert. She has shown unfailing industry, always devoting herself conscientiously to any tasks. She is very serious minded and mature. No one has been able to find any fault with the quality of her work, since it has always been painstaking and thorough as a result of her patient, unwavering application. And she has fully average ability intellectually. We could strongly recommend her for bibliographical research work, as she has had much varied experience of the right sort. It would, however, be unfair that anyone should employ her without being informed of a very evident eccentricity of character, manner and appearance, such as could make a personal conference desirable. When she could work largely by herself and when results would be the main considerations, she can render valuable service. University professors engaged in research work and in constructive writing, have found her a capable and satisfactory assistant. And she is far better equipped for such work than for those phases of library work in which she would have to deal with the general public. Still [*sic*] she is not all ignorant of library methods, having taken the full course in library economy (5).

These and other letters most likely prevented Marion Sparks from gainful employment elsewhere at a time when women were just starting to garner respect and higher positions in the field of librarianship. These references demonstrate a personal bias of Katherine Sharp since several of the letters compare Marion Sharp's attractiveness or being pretty to other recent graduates, who are generally regarded with less scholarly achievements but "prettier" or with "charm". Through the lens of the 21st century, we are more attuned to noting such discrimination as it appeared in past centuries. However, it is disheartening that Katherine Sharp decided to devalue Marion's scholarly achievements and favor looks and diminutive personality as society dictated for women at the start of the 20th century. Fortunately for Illinois, Marion Sparks decided to stay in the area and become an integral part of the Department of Chemistry.

Chemistry Library

In 1892 the Chemistry Library became the first departmental library on the University of Illinois campus. Due to limited hours and the library policy to not allow books to be taken to other buildings, various chemistry faculty, including the department heads of the time (Professors Arthur Palmer and Samuel Parr), began significant dialogs regarding permissions to borrow chemistry sources on their personal accounts from the Main Library and stored them in a secured room in the Chemistry Laboratory building. Access was limited to faculty and graduate students with assigned keys. Having access to the chemical information necessary to conduct experiments and prepare laboratory assignments was crucial, particularly when the Main Library was closed. Materials were returned at the end of each academic year. Eventually periodicals were also transferred to the new "library" space (6).

The concept of discipline-based departmental libraries being assembled in related academic buildings was becoming a new model for library services. This became a trend with academic libraries at the turn of the 20th century when there was more focus on effective educational and ready access to previous physically distant collections rather than traditional conservation and strict regulation of library materials (7). Many other subject libraries on the Illinois campus followed this model in discipline buildings with a physics branch library opening in 1909 and an engineering branch in 1916.

With her experience as a bibliographer for the Nutrition Investigation Laboratory on campus, Marion Sparks began a complete catalog of authors and shelf list of chemistry library materials in 1910. This would ultimately be the first chemistry library catalog, including author, subject, and classification of all chemistry books on campus. In 1911, she was hired as a library assistant in the chemistry library; in 1913, she would earn the title of Chemistry Librarian, a position she held until her death.

Marion was responsible for major expansion of the Chemistry Library's collection. At the start of 1916, there were approximately 100 journal subscriptions, 4000 bound serial volumes and 2900 books totaling 6900 volumes in the Chemistry Library (8). By 1927, the chemistry collection had proliferated to a total of 13,100 volumes comprised of 250 journal subscriptions with 7500 bound periodical volumes and 5600 books (9).

Sparks was a holistic librarian, involved in every aspect of library service. With her strong background in

languages and her broad interest in the sciences (including being an amateur astronomer and bird watcher), Miss Sparks was welcomed into the Chemistry Department. She assimilated quickly by providing excellent library service, including translating articles from any language, offering interlibrary loan (typewriting articles in the days before photocopiers), creating bibliographic access to materials, and conducting research.

An example of the type of research she undertook is demonstrated in the 1917 article she published in *Science* with Chemistry Department Chairman William A. Noyes, "A Census of the Periodical Literature of Chemistry Published in the United States" (10). This article is a statistical comparison of chemical research output by various institutions based on the total number of articles and total number of pages for five chemistry journals for the years 1909-10 and 1914-15. Their analysis reveals a rapid growth of chemical research from educational institutions: three fourths of papers published in 1909-10, and two thirds from 1914-15. Illinois, in fact, led the number of articles published, 45, and pages, 504, for the 1909-10 breakdown.

The following year Clarence West of the Rockefeller Institute for Medical Research used the same model to investigate publication trends in biological chemistry journals between 1907 and 1916. He also reported positive trends of increased educational institutions' contributions to the scientific literature and advocated similar publication analysis in other disciplines (11).

Chemical Literature and Its Use

Sparks' careerlong interest, however, was teaching chemical literature. In 1912, she began by giving three lectures to the Chemistry Club on library research; in 1913 she presented six lectures. During the 1914-1915 school year, Sparks began teaching "Chemistry 19," a required course for junior chemistry majors. The university first offered the class as an information seminar in 1892, becoming part of the curriculum in 1893. The original course was similar to a journal club with assigned topical readings from the current chemical literature. Marion revised the course and taught students how to retrieve chemical information.

First outlined in an article published in *Science* in 1918, Sparks compelled students to use books, reference works, and serials to the point they "know that such materials exists [*sic*] and be able to utilize it" (12). Knowing the importance of foreign chemical research, her students learned to translate research articles from German and French into English and make two speeches based on readings for the course. Sparks had students learn the most relevant indexing and abstracting resources for their specific research area. This included not only *Chemical Abstracts*, started in 1907 and by 1918 indexing nearly 700 journal titles, but foreign resources as well, such as *Jahresbericht*, the French *Bulletin, Chemisches Centralblatt* and other key resources.

In 1919, using class notes compiled from her previous six years of teaching Chemistry 19 (later required course *Chem 92*), Sparks self-published her textbook for the course, *Chemical Literature and Its Use*. She authored and published what is regarded as the first book to address chemical literature and library instruction, identifying the field of chemical information as an independent discipline (13-15). She conveyed to her students that library work was critical: locating previous research, she stressed, was as important as laboratory work. Both editions have the aphorism: "Knowing books is not enough—they must be used."

The 1919 edition, comprised of 12 lectures, introduced how libraries were arranged with the classification schemas including an explanation of how subjects were grouped and call numbers were structured. This, in turn, would enable students to easily locate relevant subject materials within the physical library space. At the time, the Dewey classification schema was used in public, academic, and corporate libraries so these information seeking skills were transferrable to other environments in which students would eventually work.

Descriptions of various chemistry societies in the United States, England, Germany, and other countries with their respective key publications were next discussed. The remainder of the book was a series of lectures on various sub-disciplines, with major reference books and journals, often by language. Careful explanations how reference resources could be utilized for nomenclature, formula, or compound searching were especially instructive.

A second edition, also self-published and self-distributed, was produced in 1921. This edition had grown to 16 lectures with new areas: searching organic chemical patents, large and small data tables, a bibliography, and new books and serials. Discipline lectures also included lists of both comprehensive and briefer descriptive works. Lecture 16 is titled, "Suggestions upon looking up all the literature for a topic in organic, applied, physical chemistry or biochemistry." It outlines, by discipline and

chronology, essential books and journals for an exhaustive chemical literature review.

Chemists in England and Australia purchased copies, as did many large chemical companies in America. A very positive review of the second edition was published in the 1921 *Journal of the Society of Chemical Industry,* including the following excerpt (16):

> A careful perusal of the pamphlet leaves the impression that the chemistry students of Illinois University are, indeed, fortunate in having the opportunity of attending this course of lectures…. Students of chemistry everywhere will find the pamphlet very useful for the purpose of reference….. The absence of systematic instruction in the consultation of the chemical literature is a fault of academic training which should be remedied. The process by which the chemist becomes familiar with the literature is comparatively lengthy, and circumstances may conspire to keep below his horizon publications which would prove of great value to him; a little systematic training … together with some instruction in indexing, would eventually save him much time and minimise the possibility of such undesirable incidents.

Sparks and Her Students

Sparks was greatly cherished by her students. Throughout her time at the chemistry library, she formed close relationships with her patrons. She corresponded with chemistry students who served in World War I and reported on their progress (and often their deaths) in the quarterly published *Illinois Chemist* (17), a departmental magazine. She also took pictures of graduating chemistry students and put them in a book of photographs. She played a pivotal role in recording the department's history as well as personal histories of its many members. Her wisdom and helpfulness for students is acknowledged by the tongue-in-cheek pseudonym "Ben Zeen" in the 1915 *Illinois Chemist*, reprinted below (18).

Arnold O. Beckman, future inventor of the pH meter and founder of Beckman Instruments, was the student editor of the *Illinois Chemist* in 1922. In it he wrote a brief editorial praising Marion Sparks and the new additions both in collections and facilities asserting it to be "one of the finest chemistry libraries in the world. With its eleven thousand volumes, endless periodicals and foreign journals, it is one to be proud of, to be treated well" (19).

Sparks remained Chemistry Librarian until her death on Sunday, February 10, 1929, following a major operation. She is buried in West Unity, Ohio, with her parents. Following Sparks' death, the university formed the Sparks Memorial committee, which created a plaque in her honor. It reads, "She was their guide when they sought information but they remember her best because she remembered them and was their cheerful mentor,

A Word to Junior Chemists

By Ben Zeen

Unwise indeed are you junior chemist, if you do not cultivate early and assiduously the acquaintance of Miss Sparks, our genial librarian. She is the sole guide and mentor of the junior along the rocky path of Chem 92. Tell her all your troubles; her only joy in life is in helping you. If you cant' find Weissnichtwohlski's article on monomethyltriphenylterabutylhexabromothiocarbamic acid, don't look in the indexes; ask Miss Sparks. If you can't spell hypocotyledonous, don't look in the dictionary; ask Miss Sparks. When you come to one of Kopp's long-winded spasms—one of those where he started a sentence and forgot to end it till his ink-horn ran dry—don't try to unravel it yourself; take it to Miss Sparks. She has nothing to do but answer questions for you; she is never happy except when she is telling some junior where she keeps Beilstein, or how to use the card catalog. She never gets tired nor hungry nor sleepy; helping juniors is rest and refreshment and repose for her. Bear these things in mind, and never lose an opportunity to ask a question.

counselor and friend." Originally made in 1930, the plaque was exhibited at that year's ACS Meeting in Atlanta and remains prominently displayed in the University of Illinois Chemistry Library today.

***Figure 2**. Plaque in the Chemistry Library dedicated to Marion Sparks.*

Legacy

Marion Sparks' legacy continues to this day. In 2001, the Chemistry Division of the Special Libraries Association (SLA) began the Marion E. Sparks Award for Professional Development. The award is intended to encourage new or student members to attend the annual meeting and participate in their activities. The monetary award helps offset the awardee's costs for attending the meeting, including registration, travel, and other expenses. Winners also receive a certificate of achievement (2).

As part of the 2002 ACS National Historic Chemical Landmark recognition, Illinois' Noyes Laboratory (originally Chemistry Laboratory) celebrated its Centennial year. Marion's contributions to chemical literature and teaching the importance of research skills were highlighted amongst achievements of notable Illinois chemists and chemical engineers (20).

In 2004, to commemorate the addition of the ten-millionth volume to the Illinois library collection, a special tome was created chronicling the personal stories of people who made and continue to make the UIUC Library what it is today. Titled *Unlocking our Past, Building Our Future: A Commemorative Publication Celebrating the University of Illinois Library at Urbana-Champaign as Resource, as Place, and as Experience*. This volume includes Marion's creation of *Chemical Literature and Its Use* and her contribution to chemistry literature research.

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About the Authors

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2022 HIST Award

The winner of the HIST Award for Excellence in the History of Chemistry for 2022 is Marco Beretta of the University of Bologna for his leadership in the history of the materiality of chemistry. Professor Beretta received his BA with honors in the History of Science from the University of Milan in 1986. He proceeded to the Department of the History of Science and Ideas at Uppsala University. An early sign of things to come was the Partington Prize received in 1990 for his essay in *Ambix*: "The Historiography of Chemistry in the Eighteenth Century: A Preliminary Survey and Bibliography." He received his Ph.D. degree from Uppsala in 1994 for his thesis: "The Enlightenment of Matter: The Definition of Chemistry from Agricola to Lavoisier." This work was awarded the Johan Nordström and Sten Lindroth Prize and the Prize for young historians of the International Academy of History of Science. He returned to Italy as a research fellow at the Museo Galileo in Florence in 1994. He joined the University of Bologna in 2000.

While at the Museo Galileo, Beretta compiled a critical catalog of the library of Lavoisier: *Bibliotheca Lavoisieriana*. His fascination with Lavoisier resulted in an important monograph, *Imaging a Career in Science: The Iconography of Antoine Laurent Lavoisier* (2001). He is a leading Lavoisier scholar and since 1994 has been a member of the Comité Lavoisier (the Comité was the recipient of the Franklin-Lavoisier prize in 2018).

Beretta is a leading scholar of the history of glass in art and technology. He received the Paul Bunge Prize for his monograph *The Alchemy of Glass* (2009). He combines the full range of appreciation for the artifacts of science: curation, history, display, contextualization and artistic importance.

He has become a highly sought-after editor and collaborator for important publications in the history of science. He was the Editor of the journal *Nuncius: Journal of the Material and Visual History of Science.* Most recently, he is editor of volume I of the six-volume Bloomsbury *Cultural History of Chemistry*. He is considered one of the leading scholars on ancient chemistry and has helped to create a vibrant research field of young and productive scholars.

IRWIN B. WILSON (1921-2013): THE STORY OF THE FIRST RATIONAL DESIGN OF A DRUG

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Abstract

This article is based upon a lecture that Irwin Wilson (Figure 1) gave for his 75^{th} birthday on September 18, 1996. (His actual date of birth was May 8, 1921.) The lecture covered his early work on how acetylcholinesterase catalyzes the hydrolysis of acetylcholine. This led to his demonstration of the formation of a covalent acetyl-enzyme intermediate in the reaction. It should be noted that this was in the days before it was understood that an enzyme could catalyze a chemical reaction by forming a covalent intermediate. Further studies on the mechanism of acetylcholinesterase in his laboratory at Columbia University in 1956 gave rise to the rational design of Pralidoxime (2-pyridine aldoxime methyl chloride; 2-PAM) as a reactivator of the organophosphate-inhibited enzyme. Dr. Wilson's picture at the time of this discovery is shown below.

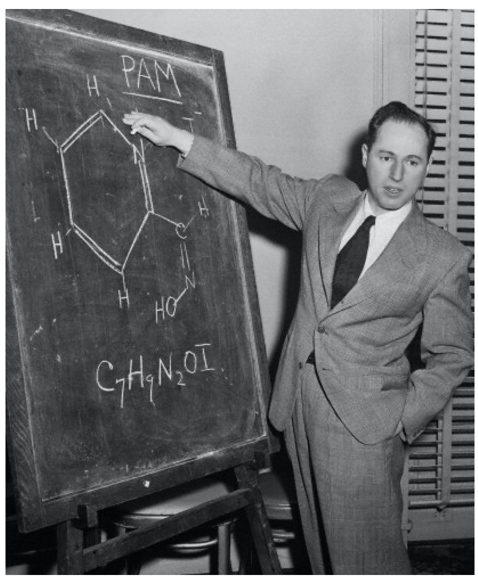


***Figure 1**. Irwin Wilson at the time of his work on acetylcholinesterase. (Courtesy of the Wilson family)*

Introduction

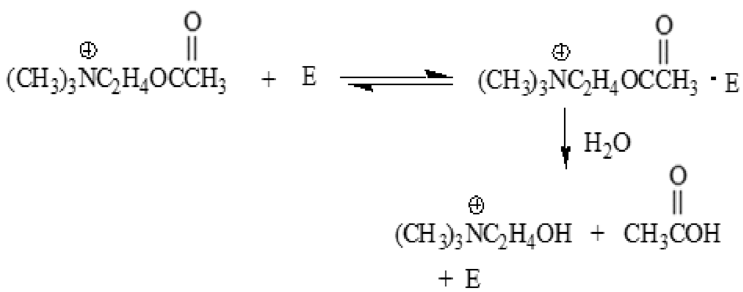
After World War II the military recognized that nerve gas was still a problem and there were rumors that the Russians were stockpiling it. Poisoning by the types of organophosphates that includes nerve gases and insecticides was a serious problem and a method of correcting this problem was needed. These compounds are very toxic because they are potent inhibitors of the enzyme acetylcholinesterase, and thereby prevent the clearing of acetylcholine from cholinergic neuro-muscular junctions. Thus, the American military was interested in funding research on antidotes to this type of poisoning.

The military flew a special plane to South America to obtain electric eels (not actual eels but more closely related to carp and catfish) because they contain large amounts of acetylcholinesterase. They were used for the project at Columbia. This allowed the researchers (listed below) to isolate and purify the protein to crystalline form for the first time.

These studies on acetylcholinesterase which led to the first rationally designed drug were carried out in Wilson's laboratory at Columbia University in the 1950s. Wilson acknowledged he had many gifted collaborators who he said were fun to work with. Some of those involved with cholinesterase at Columbia were Felix Bergmann, David Nachmansohn, Sara Ginsberg (an organic chemist trained in Russia, who played a big part in the synthesis of the new compounds), Estella Meislich, Enrico Cabib, Richard Kitz and Richard Epand.

Acetylcholinesterase

The mechanism for an enzyme-catalyzed reaction by acetyl cholinesterase is seen in the Michaelis-Menten scheme below where acetylcholine is shown forming a complex (seen as a dot) with the enzyme (E) leading to the breakdown to choline and acetate:



Wilson investigated the "dot" in the Michaelis complex (the binding features between the enzyme and the substrate) mostly by studying reversible inhibitors. He concluded that the binding features were electrostatic forces, hydrocarbon-hydrocarbon interactions, hydrogen bonds and **nucleophilic addition to the carbonyl carbon**.

The Anionic Site

Wilson showed that cationic compounds were bound to acetylcholinesterase as much as 30 times better than neutral analogous inhibitors and substrates (1-3).

Prostigmin (neostigmine), a carbamate with a quaternary ammonium function, inhibits the action of nerve gas to the same extent in the pH range 6-10; however, physostigmine with a tertiary ammonium function, pKa ~ 8.5, inhibits less as the pH is raised (Figure 2) and the charge diminishes.

Similarly the rate of hydrolysis of dimethylaminoethyl acetate, pKa ~8.5, declines as the pH is raised.

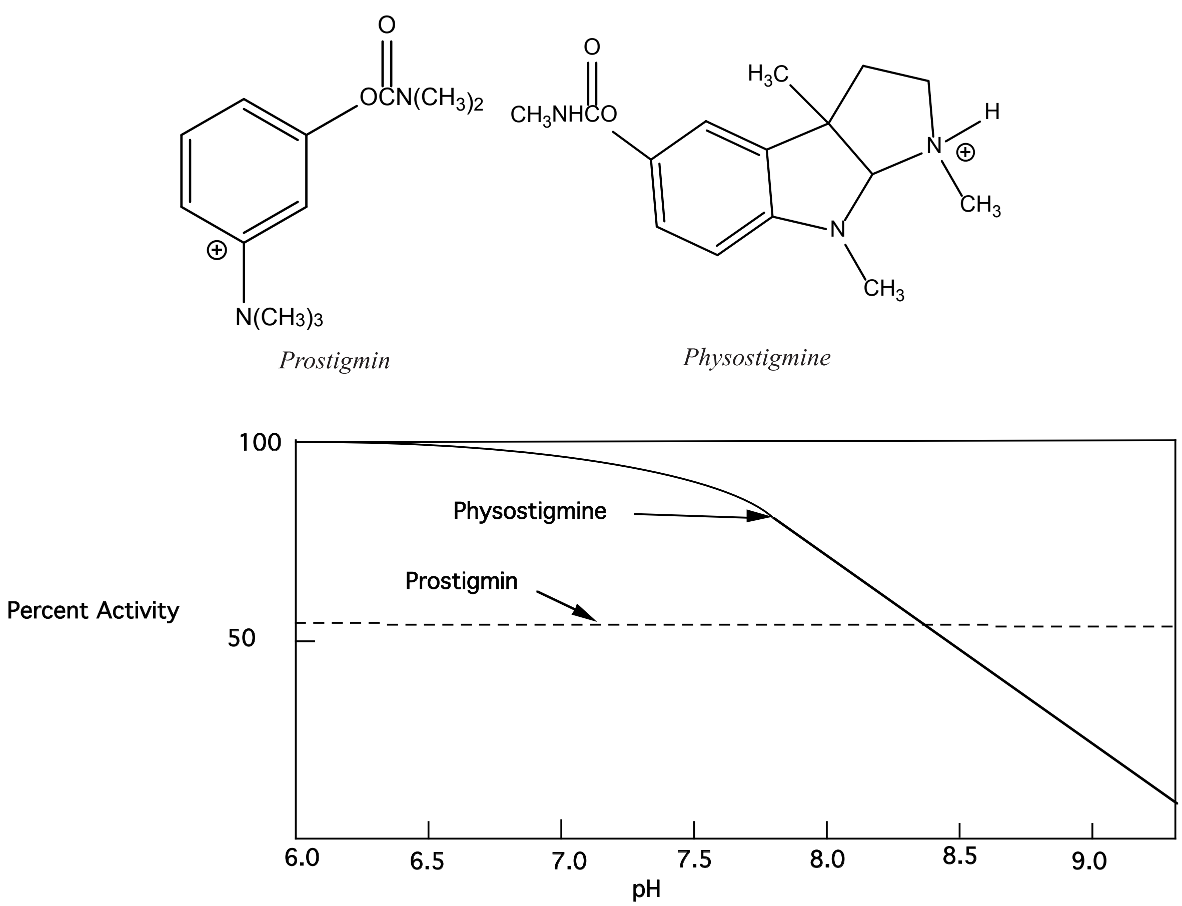


Figure 2. *Structures of prostigmin (neostigmine) and physostigmine and their inhibitory activity as a function of pH (after Figure 1 of Ref. 1).*

dimethylaminoethyl acetate   isoamylacetate

In its charged form dimethylaminoethyl acetate is a better substrate than isoamylacetate, but the uncharged form has a comparable reaction rate to isoamylacetate.

Similarly, choline, $(CH_3)_3N^+C_2H_4OH$, is 19 times more potent as an inhibitor than its carbon analogue $(CH_3)_3CC_2H_4OH$, and dimethylaminoethanol ammonium ion $(CH_3)_2NH^+C_2H_4OH$ is 30 times more potent than isoamylalcohol $(CH_3)_2CHC_2H_4OH$.

Wilson took this data to mean that the substrate had to have a charge in order to be attracted to the active site of the enzyme and thought that the electrostatic contribution to binding these two cationic (positively charged) inhibitors might derive mostly from a carboxyl group of the enzyme falling close to the cationic group, because the calculated effect using an empirical formula is in quantitative agreement with these observations.

Adams and Whitaker (4) had earlier argued for an electrostatic contribution of binding. Later measurements (5), with a genetically engineered enzyme in which a pertinent glutamic acid in the active site is replaced by glutamine, support the role of this glutamic acid as the major source of the electrostatic potential. In these later studies, the binding of 3-hydroxyphenyl-trimethyl ammonium ion, which is an active site specific inhibitor, is reduced by a factor of 19, and k_{cat}/K_m (which is the efficiency with which an enzyme converts a substrate into a product) is reduced by a factor of 50 due to this mutation (5). This verified Wilson's earlier thoughts.

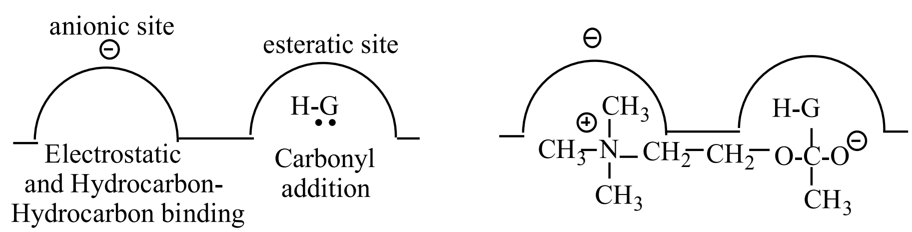


***Figure 3**. Schematic picture of the active site of the cholinesterase enzyme.*

Hydrocarbon Contacts

The binding of ammonium ions is progressively diminished as methyl groups are "removed" from tetramethyl ammonium ion: $(CH_3)_4N^+$ is 3 times better than $(CH_3)_3NH^+$, 21 times better than $(CH_3)_2NH_2^+$ and 140 times better than $(CH_3)NH_3^+$. The binding of NH_4^+ is too weak to measure. The binding of phenyl-trimethyl ammonium ion is 100 times better than $(CH_3)_4N^+$.

Wilson attributed the effect of each methyl group to hydrocarbon-hydrocarbon contacts between the inhibitor and the enzyme analogous to the forces holding methane molecules in contact in liquid methane. The value for the heat of evaporation of methane is reasonably appropriate (The concept of hydrophobic interactions had not yet been advanced). More recent x-ray studies by others validate Wilson's thinking, by showing that the substrate lies in a hydrophobic groove in the active site (6).

Nucleophilic Addition

The pH curve of enzyme activity can be fitted with 2 pKa values, 7.2 and 9.5 (1).

$$EH_2^{\oplus} \overset{7.2}{\rightleftharpoons} EH \overset{9.5}{\rightleftharpoons} E^{\ominus}$$

Inactive Active Inactive

The first ionization corresponds to the imidazole group of histidine. A carbonyl group contributes to the binding of some inhibitors, and Wilson thought imidazole might be the enzymic nucleophile and add to suitable carbonyl groups. Of course, it is now known that the hydroxyl group of serine, which is labeled with diisopropylflurorphosphate (6), is the enzymic nucleophile while imidazole has an essential role as a general base-general acid catalyst (7).

Wilson drew a schematic picture of the active site of the enzyme (Figure 3) using the noncommittal symbol G for the nucleophile and showing that the enzyme's active site consists of two subsites.

The Acetylenzyme

Based upon the results above, Wilson (8) speculated that the enzymic hydrolysis of esters (the forward reaction) might take place in two steps with an acetylenzyme as an intermediate.

Whatever the mechanism, the presence of this common intermediate on cholinesterase means that the enzyme must also be able to synthesize acetylcholine from acetate and choline (i.e., catalyze the reverse of hydrolysis) to an extent depending on the free energy change in the reaction). This fits with previous studies that showed that the enzyme also synthesizes acetohydroxamic acid from acetate and hydroxylamine (9, 10).

Wilson thought that if acetylenzyme were an intermediate, the formation of acetylcholine or acetohydroxamic acid would surely occur much more rapidly using ethyl acetate instead of acetate because the ethyl moiety would be a better leaving group. This proved to be the case, and the rates were 150-300 times faster. These observations rule out the possibility that the hydrolysis of ethyl acetate provides acetate for the reaction and indicate that a transacylation reaction occurs that is readily explained by the formation of an acetylenzyme.

It is apparent that a necessary condition for this theory is that a series of acetate esters (with different alcohol residues) must in the presence of hydroxylamine produce the same ratio of acetohydroxamic acid to acetic acid. Similarly, in the presence of choline, the ratio of acetylcholine to acetic acid should be the same for each ester. (These reaction pathways are shown in Figure 4.) This argument was later tested with α- and γ-chymotrypsin using eleven different esters of hippuric acid (11). The fraction of ester converted to hippurylhydroxamic acid was the same for each of the eleven hippuric acids, within a precision of 1% and different for the two different chymotrypsins. On the other hand, if the ester portion is held constant, with ethyl esters of five phenyl-substituted hippuric acids the ratios were found to be very different. Similarly, the ratios were very different for the non-enzymic hydrolysis by hydroxaminolysis of these same hippuric acid esters.

These results are a sufficient condition for proving a common intermediate because a constant ratio of products does not otherwise happen in chemical reactions. Thus, these results provided the first evidence of a covalent enzyme substrate intermediate for the acetylcholinesterase catalyzed hydrolysis.

The two-step process was also supported by the finding that the Arrhenius plot for acetylcholine was curved, indicating two rate-influencing steps with different energies of activation, steps that Wilson took to be acetylation and deacetylation of the enzyme. Since N-methylaminoethyl acetate and aminoethyl acetate are much poorer substrates, there should be only one rate influencing step (acetylation), and the Arrhenius plots for these substrates were straight.

From the formation of an acetylenzyme one can predict that acetylcholinesterase will catalyze the exchange of oxygen between acetate and water. Wilson showed this indirectly by using sulfur as a marker for oxygen and demonstrating that the enzyme hydrolyzes thiol acetic acid (CH_3COSH) (12). The hydrolysis of thiol acetic acid to produce H_2S is analogous to oxygen exchange. Later others demonstrated the exchange using ^{18}O water (13).

Organophosphates (Phosphonates)

The organophosphate inhibitors of acetylcholinesterase (Figure 5) have a good leaving group, including F^-, Cl^-, CN^-, nitrophenolate, $-SC_2H_4{}^+N(CH_3)_2$, diethyl phosphate, etc., and 100 more, which allows the organophophate act as a phosphorylating agent and to covalently react with an active site reactive group.

Usually replacing EtO- by CH_3- increases the rates of inhibition. Potency generally refers to the rate of inhibition, i.e. the second order rate constant. Many of these compounds form reversible complexes with the enzyme prior to phosphorylation.

These compounds are phosphorylating agents and Wilson was confident that they phosphorylated the same nucleophilic group that is acetylated during the hydroly-

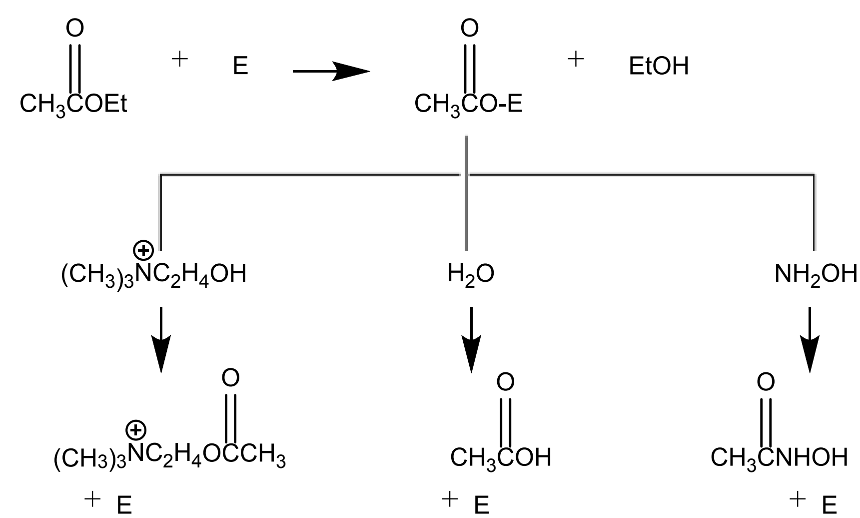


Figure 4. Pathways for reactions of choline, water and hydroxylamine via an acetylenzyme.

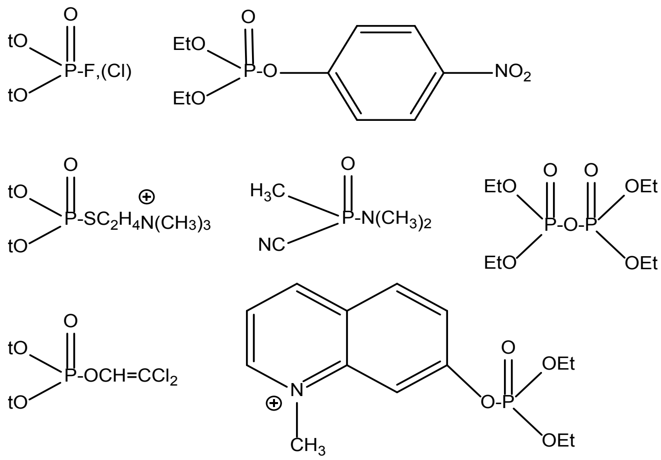


***Figure 5**. Examples of organophosphate inhibitors of acetylcholinesterase.*

sis of esters. He supported this idea by showing that the pH curve for inhibition with tetraethyl pyrophosphate was the same as for the hydrolysis of β-bromoethyl acetate (data not published). Others later showed more conclusively that the enzyme is phosphorylated by these inhibitors (14).

By analogy with the acetyl-enzyme, Wilson thought that the phosphoryl enzyme should react with hydroxylamine, choline and water (Figure 6). He found he could demonstrate the reactivation of the inhibited enzyme by these reagents.

His studies on this reactivation and the following design studies are found in a series of papers summarized below (15-20).

Hydroxylamine has two nucleophilic centers N & O, and he determined that it was the oxygen center that was important for reactivating the enzyme by finding that N,N-dimethylhydroxylamine was active but O-methyl hydroxylamine was not; trimethylamine oxide was also active.

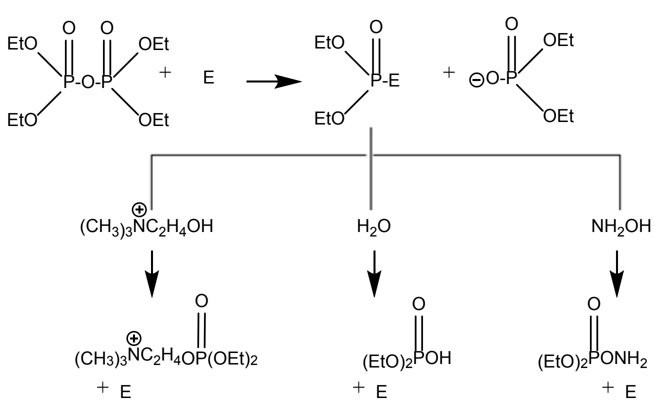


***Figure 6**.. Pathways for reactions of choline, water and hydroxylamine via a phosphoryl enzyme.*

H_2NOCH_3	$(CH_3)_2NOH$	$(CH_3)_3\overset{\oplus}{N}\text{-}\overset{\ominus}{O}$
Inactive	Active	Active

Hydroxylamine is a very good nucleophile but choline [$(CH_3)_2NOH$] is not. Yet choline does reactivate the enzyme. He thought that choline was active because it was bound at the anionic site, which would still exist in the phosphoryl enzyme. However, the binding of choline to the phosphoryl enzyme is 100 times weaker than to the free enzyme. Reactivation can be prevented by tetramethyl ammonium but again binding by this ion is poor. He thought the poorer binding was the result of steric hindrance.

The concentration dependence (Figure 7) shows the formation of a complex for choline but not for hydroxylamine:

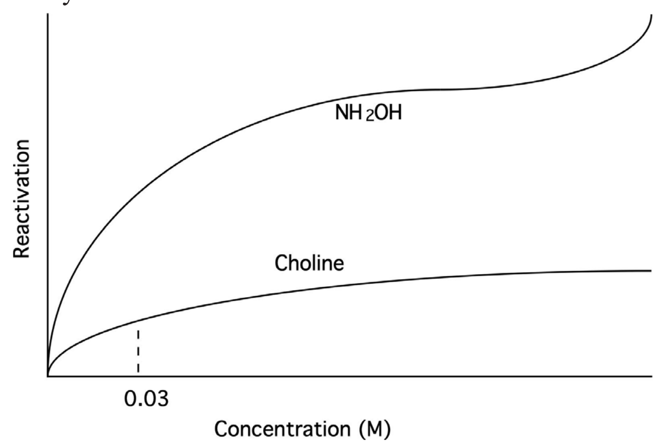


***Figure** 7. Concentration dependence of enzyme reactivation by choline and hydroxylamine, after Figure 1 of Ref. 15.*

Wilson believed he might be able to make a very good reactivator by combining a good binding structure such as the compounds in Figure 8, with a good nucleophilic group based on hydroxylamine. He tended to favor pyridine derivatives because he thought there might be less steric hindrance than in phenylamines.

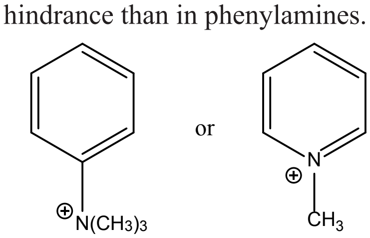


***Figure 8**. Trimethylphenylammonium (left) and* N-*methylpyridinium (right) ions.*

Although the organophosphate inhibitors were considered irreversible inhibitors, Wilson reasoned the following: The reaction with the enzyme is of course reversible in principle and any leaving group should be a reactivator but reactivation may be negligible depending upon the equilibrium constant and speed of the reaction; chloride is not a reactivator but fluoride is. Actually, there are lots of reactivators and in principle the diethylphosphoryl derivative should be an inhibitor but again that will be determined by the equilibrium constant and speed of the reaction. Diethylphosphoryl choline is not an inhibitor, but diethylphosphoryl-2PAM (Figure 9) is a very potent inhibitor (21).

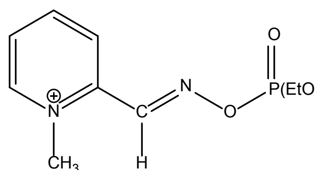
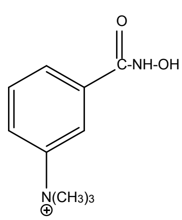


***Figure 9**. Diethylphosphoryl-2PAM.*

Synthesis of Better Reactivators

One of the first compounds he made was the hydroxamic acid,



which proved to be much better than acetylhydroxamic acid or hydroxylamine but far short of what he was seeking. He was looking for more spectacular results as illustrated in the sequence shown in Figure 10.

In the series illustrated in Figure 10, the starting oxime is much better than hydroxylamine and the quaternary product is thousands of times better (21). Since the pKa values of these reactivators are about the same it seems likely that their intrinsic nucleophilicities are not very different. In fact, they reactivate phosphorylated chymotrypsin (which does not have an anionic binding site) at the same rate but of course much more slowly than they reactivate cholinesterase.

The binding of the reactivator is not of any value *per se*. It will be helpful only if the reactivator forms a highly productive complex—one in which the nucleophilic oxygen is located at about one bond length from the phosphorous atom and directed at the proper angle for mounting a nucleophilic attack. (Also a poorly productive complex that is far more stable should not be possible.) Thus, he reasoned that if the reactivator formed a productive complex with a "floppy" reactivator there may be a large loss of entropy in forming the more rigid "productive" complex. Thus, he wanted to have a fairly "rigid" reactivator with the right configuration. He thought the pyridine aldoximes offered the hope of finding a super reactivator since there are six isomers available (in principle): three positions in the ring and syn-anti pairs (Figure 11) (22).

From observations with carbamates he thought 2-PAM-anti might be a spectacular reactivator and he erroneously thought that 2-PAM had the anti configuration because treatment with acetic anhydride yielded the nitrile: this is a "textbook" method for assigning anti configurations. However, others showed by NMR, X-ray diffraction and molecular modeling (23-25) that 2-PAM had the syn configuration. Anti 2-PAM was not made and its ability to serve as a reactivator is not known.

He did a few experiments with mice using 2-PAM as an antidote against organophosphate inhibitors. 2-PAM with and without atropine, was remarkably effective against the organo-phosphate paroxon. Atropine protects muscarinic acetylcholine receptors. Table 1 shows toxicity data for 2-PAM and paraoxon (21). Table 2 shows partial results from treatment experiments against paraoxon (21)

***Table 1**. Toxicity data for 2-PAM and paraoxon in mice.*

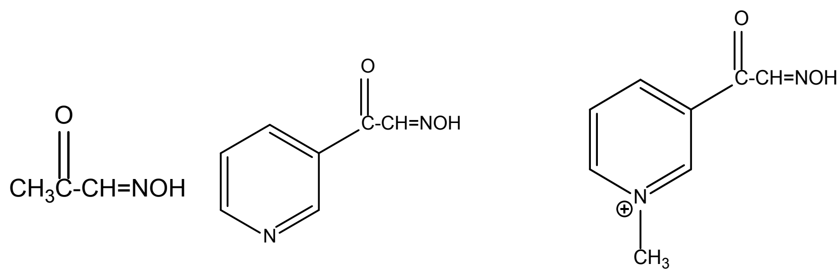
2-PAM	paraoxon
LD_{50} 136 mg/kg	LD_{50} 0.7 mg/kg
LD_{100} 190 mg/kg	LD_{100} 0.9mg/kg
Probable safe dose = 100 mg/kg	

Very good results were obtained against tetraethyl pyrophosphate and diisopropyl fluorophosphate. Against sarin results were very much poorer but still all mice survived an LD_{100} injection.

***Table 2**. Partial results from treatment experiments against paraoxon in mice.*

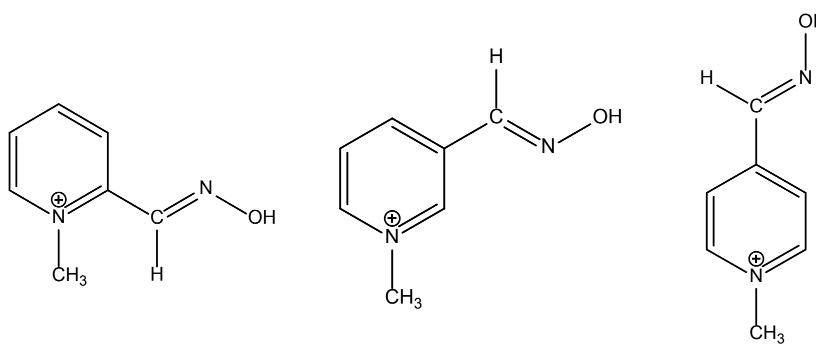
Atropine mg/kg	2-PAM mg/kg	Paraoxon Multiple of LD_{50}	Number of Mice	Number of Survivors
0	0	1.0	10	5*
0	75	1.0	10	10
0	0	1.3	10	0*
0	30	1.5	20	20
10	0	5.0	5	0
10	50	15	20	20

*Confirms previously obtained LD_{50}, LD_{100}.



$3\ M^{-1}\ min^{-1}$ $83\ M^{-1}\ min^{-1}$ $2500\ M^{-1}\ min^{-1}$

***Figure 10**. Inhibition rate constants for successively derivatized oximes.*



2-PAM 3-PAM 4-PAM

$\sim 10^6 \times NH_2OH$ poor $\sim 2\times10^4 \times NH_2OH$

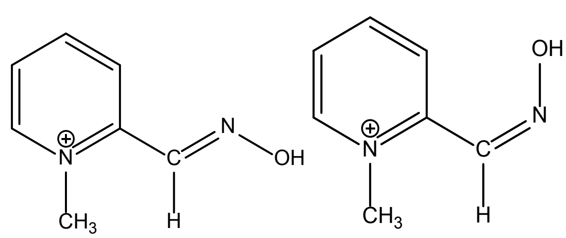


***Figure 11**. Isomers of pyridine oximes differing in position of the oxime group (above) and in configuration (below). The positional isomers are all syn; the numbers show relative activity. The configurations are syn (left) and anti (right).*

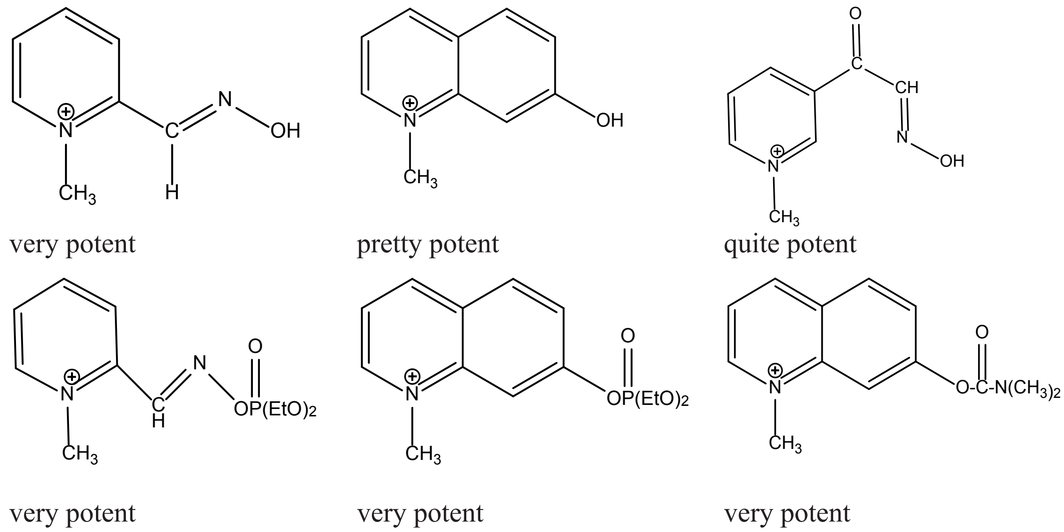


Figure 12. *Potency of activators (above) and inhibitors (below).*

In retrospect, it is interesting to note the similar configurations of some potent reactivators and inhibitors as shown in Figure 12 (21). Of course, not all observations fit this pattern readily.

Conclusions

What Wilson showed for the first time was that an enzyme can form a stable covalent intermediate in the catalysis of a chemical reaction. In addition, Wilson was able to use these mechanistic studies to rationally design a drug that could be used to treat a person poisoned by a nerve gas or an insecticide that reacts with acetylcholinesterase. 2-PAM became the go-to drug for this type of treatment at that time in history.

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FREEING THE MOLE FROM THE KILOGRAM: HOW THE REDEFINITION OF THE KILOGRAM SHAPED OUR DEFINITION OF THE AVOGADRO NUMBER

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Abstract

An update to the scientific system of measurement went into effect on May 20, 2019, redefining the mole and the kilogram, along with the ampere and kelvin. These units follow the meter, candela and second to be defined by fundamental universal constants. The update to the kilogram is most symbolic, because it renders obsolete a metal cylinder kept in a vault near Paris that has defined the kilogram for 130 years and is part of a long history to search for a standardized system of measurement that would span across cultures and prove reliable and replaceable if destroyed by war, fire or other disaster. An update to the kilogram necessitates an update to the mole since historically the two have been intimately linked. Most people will never notice the change, but just below the surface, it represents a significant breakthrough in our relationship to base units of measurements and the Avogadro constant. This paper explores the origins of some widely used units, followed by an overview of standardization and the metric system, and finally the development of our current value for the mole and how it is tied to the most recent revisions to the International System of Units (SI).

Why a Standard

In 1958, as part of a fraternity stunt, a group of students measured the Harvard Bridge using one of their members, Oliver R. Smoot (5′ 7″) as the ruler (1, Figure 1). The result was 364. 4 Smoots "plus or minus one ear." This stunt, while meant in jest, highlights the variety of units of measurement. A reliable form of measurement must be accessible in the environment, of appropriate scale for the intended measurement and it must be reliable. Prior to the industrial revolution, societies developed their own measures as varied as their cultures and politics. Yet, with the advent of the metric system, nearly every country has adopted one consolidated system of measurement in a relatively short period of time.

Figure 1. *A commemorative plaque on the history of the "Smoot" as a unit of measurement can be found on the Massachusetts Avenue bridge over the Charles River. The bridge connects Back Bay (Boston) and Cambridge, Massachusetts (Wikimedia Commons, https://commons.wikimedia.org/wiki/File:Harvard_Bridge_Smoot_plaque.jpg).*

Still the metric system had its problems. The kilogram, while accepted in the scientific community, has been historically based on a set of kilogram standards

stored and locked in a vault. Not only is the standard vulnerable to destruction from war or natural disaster, but studies show that the kilogram standard (kept just outside of Paris) had been losing mass compared to its replicas, calling into question its accuracy (2, 3).

The Oldest Measuring Instruments

Oliver Smoot and friends are not the first people to use their body or body part as a measurement standard; the human body is likely the first and oldest measuring instrument. Nearly every civilization once had a *foot* unit, often subdivided into *fingers* (4). The ancient Greeks had a foot measure (*pous*) subdivided into *dactyloi* (5). In China, the foot measure was called the *chi* and subdivided into *cun* (6). Human cultures also developed length, weight, and volume standards from grains and seeds, including rice, corn, millet, barley and carob. The human body and objects from the environment proved easily accessible and scale appropriate, but variations between individuals brought into question the reliability.

Patterns in measurement units can also assume an aesthetic and spiritual significance. Twelve times the inch makes a foot. Three times the length of the foot is the distance from the tip of a man's nose to the end of his outstretched arm, approximately a yard. The distance across a man's outstretched arms equals a fathom or two yards. The Roman architect and historian Vitruvius wrote about the dimensional relationships between parts of the human body and maintained that the proportions mirror a type of cosmological order (7):

> It was from the members of the body that they [the ancients] derived the fundamental ideas of the measure which are obviously necessary in all works.

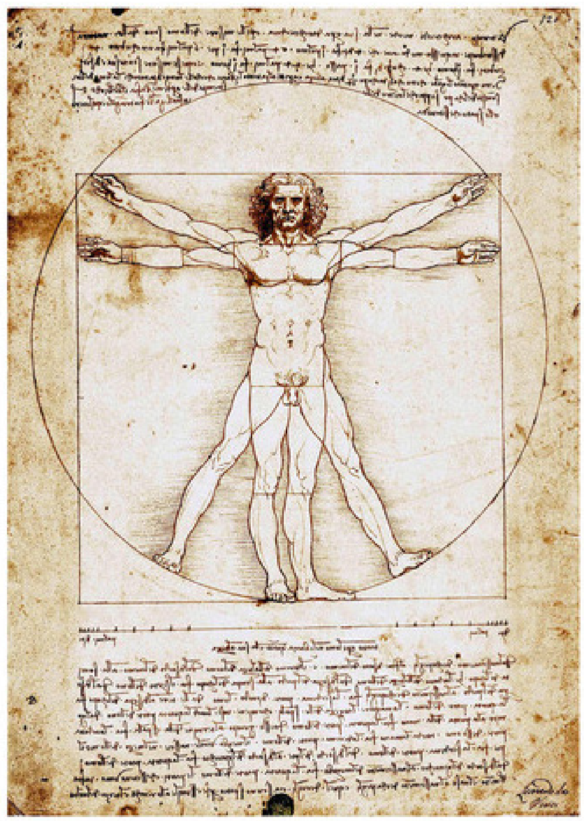

Figure 2. *Vitruvian man (c. 1490) is one of the most recognized (and most parodied) of Leonardo DaVinci's sketches. If a man is placed on his back, with hands and feet extended, a compass at the navel, his fingers and toes will touch the circumference of a circle. (Public Domain).*

Leonardo da Vinci likely had the work of Vitruvius in mind for his famous drawing, Vitruvian Man, which displays how the proportions of the human body and the units drawn from it can have symbolic and spiritual significance (Figure 2).

The Roman Empire introduced many of the basic units that we know today, such as the *Pes* (foot) for length and the *Libra* (pound) for weight (8). In France and throughout Europe, these units replaced or modified units used by the conquered inhabitants. In France, the weight measure was a *Livre*, in German, it was the *Pfund*, the Dutch called it a *Pond* and British called it a *Pound.* All were derived from the Roman *Libra*, hence the abbreviation of *lb.* for a pound. Some pre-Roman measurements persisted into the Middle Ages and different regions within a country adapted Roman units in their own way, altering the dimension and names to meet the local needs and items to be measured (4).

In rural European communities, measurements might vary from town to town. A measure of land might be for the amount of land worked in one day, which would vary according to the terrain. For example, a rocky or uneven plot of land is more difficult to prepare and sow when compared to a flat section of land with loose, workable soil. Other units grew out of transport of goods. These were based on the type of the goods, the size of the animal (or person) carrying the goods, and the distance traveled. Terms like *cartload, wagonload and boatload* were born out of a need to quantify goods (4). In feudal societies, the units even varied among social roles. In the book, *Measures and Men* (9), Kula writes:

> Within a single village, one measure was used in the market, another in the payment of church tithes and yet a third in rendering dues to the manor.

The Metric System

While there were attempts throughout European history to impose absolute standards, they rarely lasted and were mostly ignored in the rural regions. In spite of the human body being readily accessible and scale appropriate, there was still a need to select one object to define a unit of measure. If the unit is a foot, whose foot should be used? If the unit is 3 barleycorns, who selects which barleycorns are the standards? Upon creating a standard, all other measurements must be based on this one artifact. If the standard does not belong to the local environment, then it must be housed somewhere and protected, usually by those who control political and social power. Residents in rural areas would have no access to the standard and thus no motivation to use it.

This problem with standardization prompted 17th-century investigators to begin searching for universal units of measurements. Their goal was to find units that were not tied to a local environment, but could be derived anywhere on Earth. In 1662, the Royal Society of London for the Promotion of Natural Knowledge was officially incorporated, and a few years later in 1666, Louis XIV sanctioned the French Academy of Sciences. The two societies shared information and one of their goals was to develop standards using an unchanging natural phenomenon (4). It was an ambitious goal: a standard that could be re-created anywhere on the earth. At the time, there were two candidates, the seconds pendulum (a pendulum whose time is one second per swing, two seconds per period, and approximate length is 1 meter) and the earth's meridian (distance along the earth's surface between the north and south poles).

Gabriel Mouton (1618-1694) proposed a standard linear measurement called the *mille*, which was based on the earth's meridian and divided decimally. He further proposed a coordinated system of multiples and submultiples from the base unit (10). His colleague, Jean Picard (1620-1682), organized an expedition to measure the degree of arc of the meridian that passes through Paris. His new measurement was 57,060 *toises* (a pre-revolutionary French unit of measure for length). The use of a fixed standard, subject to deterioration, prompted him to measure the length of a seconds pendulum, and he found it to be 36 inches and 8.5 lines. It was imperfect due to variations in temperature and humidity.

In 1735, the French Academy of Sciences mounted a new expedition to measure the length of the meridian in Peru, close to the equator and in Lapland, close to the poles. This effort resulted in the Peru Toise (divided into 6 feet, each foot 12 thumbs and each thumb 12 lines). In 1766, eighty copies were made and sent to various places in France.

The French Revolutionary government sought to impose rational measures throughout the country. In 1791 as part of this effort, the French Academy of Sciences defined the basic unit of length as one ten-millionth of the distance from the equator to the North (or South) pole. The length unit was given the name *meter* from the Greek word *metron*, meaning *measure*, and a new expedition was mounted to measure the meridian arc. The results were anticipated based on previous measurements and provisional standards were dispersed before the expedition was finished. The Academy decided that length, volume and mass units were all to be linked, with the entire system derived from one universal standard with a decimal system of length measures based on subdivisions and multiples of the meter. Pierre Méchain and Jean Baptiste Delambre were tasked with the job of measuring the meridian arc which runs from Dunkerque through Paris to Barcelona. Another committee was tasked with the precise weight of a known volume of distilled water at zero degrees Celsius. In the midst of the French Revolution with shifting political powers and brutal dictatorships, the project took 7 years to complete (10).

In 1798, at the suggestion of several Academy members, foreign delegates were invited from eleven countries known to be sympathetic to the Revolutionary government. While not open to every country, the inclusion of foreign delegates alongside French scientists "created a transition toward the modern idea of an international scientific congress" (11).

The conference in 1798-99 finalized standard measurements and explored how best to create and disseminate international standards (10). The result was the *meter*, ultimately accepted as one ten-millionth of the distance from the North pole to the equator. A measurement of distilled water was used to establish the kilogram standard. A meter bar and a kilogram standard were cast of pure platinum and became the standards for the metric system in 1799 (11).

An international transformation to standardized units of measurement began to take place haltingly through the 19th century. By the middle of the nineteenth century, the metric system was established in France and accepted by only four countries, Belgium, Luxembourg, the Netherlands and Algeria, a French colony at the time. However, by 1870, eight more countries had adopted the metric system (4). Two factors pushed the acceptance of

the metric system, the expansion of national and international markets and the demand for precision parts and tools to maintain the new industrial machines: clocks, printing equipment, cannons, engines, muskets, etc. At the time scientists struggled to find precise and consistent measures and instruments. Thomas Jefferson was unable to convince the United States (US) Congress to adopt the metric or decimal system and subsequent attempts failed as well. A century later, the failure of the US to convert to metric was painfully obvious to scientists when NASA lost the Mars Climate Orbiter spacecraft in 1999 due to data provided in English units and implementation by engineers as if it were in metric (12).

In 1870, an International Commission for the Meter, appointed by Emperor Napoleon III, was initially set to meet in Paris with twenty-five countries attending. War with Prussia adjourned the meeting for two years until France stabilized and the meeting was rescheduled (4). In 1872, representatives from thirty countries attended the International Metric Commission and proposed the establishment of an international organization called the International Bureau of Weights and Measures, or BIPM (*Bureau International des Poids et Mesures* in French). The organization was to be funded jointly by participating nations and tasked with the job of making and preserving new standards, with a General Conference of Weights and Measures (CGPM) held every 6 years. The journal *Nature* described the commission's objective as, "one of the greatest triumphs of modern civilisation" (13).

Representatives returned to their countries with a draft of the treaty to obtain permission from their governments. The International Bureau of Weights and Measures (BIPM) was officially established in May 1875 with a treaty signed by 17 participating countries. It was charged with the task of providing the basis for a single, coherent system of measurements to be used throughout the world. The international standards for the meter and kilogram were based on the decimal metric system dating from the time of the French Revolution. New standards for the meter and kilogram were manufactured and formally adopted by the first CGPM in 1889 (14).

Since 1889, the SI unit of mass, the kilogram, has been defined as being equal to the mass of the international prototype kilogram (IPK), a cylinder of platinum-iridium alloy. The prototype is housed at the BIPM outside of Paris. When the prototype was created, identical prototype cylinders were distributed to countries around the world. Over time, the original prototype has lost mass when compared to the prototypes housed in other locations. Stephan Schlamminger, a physicist at the US National Institute of Standards and Technology summarized the problem as follows (15),

> If aliens ever visit the Earth, what else would we talk about other than physics? If we want to talk about physics we have to agree on a set of units, but if we say our unit of mass is based on a lump of metal we keep in Paris, we'll be the laughing stock of the universe.

The Mole and the Kilogram

Many people are surprised to learn that Amedeo Avogadro (1776-1856) did not discover Avogadro's number (N_A). He was, however, the first to propose that equal volumes of different gases at the same temperature and pressure contain the same number of particles. In 1865, Austrian scientist, Josef Loschmidt, used kinetic molecular theory to estimate the number of particles in one cubic centimeter of gas at standard conditions. Then in 1909, French physicist Jean Baptiste Perrin introduced the term Avogadro's constant for the number of molecules in a gram-molecule. (Chemists usually call this quantity Avogadro's number. A gram-molecule is now called a mole.) Perrin determined an estimate of Avogadro's number ($N_A \approx 7.05\times10^{23}$ mol^{-1}) based on his work on Brownian motion, the random movement of microscopic particles suspended in a liquid or gas (16, 17).

Other methods gave similar values. American physicist Robert Millikan's (1868-1953) famous oil drop experiment determined the charge on an electron (now fixed at $1.602176634\times10^{-19}$ C). The charge on a mole of electrons (95,485.33 C, Faraday's constant) had been known for some time. Dividing the charge of a mole of electrons, Faraday's constant, by the charge of a single electron gave Avogadro's constant (Equation 1). Millikan's value was, $N_A \approx 6.064\times10^{23}$ mol^{-1} (18). Based on the work of Rutherford with alpha particles, Avogadro's constant could also be determined by the counting of alpha particles emitted from radium or uranium: $N_A \approx 6.16\times10^{23}$ mol^{-1} (19).

$$\frac{96485.3\ \mathrm{C\ mol^{-1}}}{1.602177\times10^{-19}\ \mathrm{C}} = 6.02214\times10^{23}\ \mathrm{mol^{-1}}$$

Equation 1. *Dividing the charge of a mole of electrons, Faraday's constant, by the charge of a single electron gives Avogadro's constant,* N_A*. These values are based on current National Institute of Standards and Technology (NIST) numbers (https://physics.nist.gov/cuu/Constants/index.html).*

Another approach to determine Avogadro's number started in 1913 with Bragg's studies on x-ray crystal dif-

fraction (20). Physicists found they could compare the density of a material with x-ray diffraction data which gave the number of atoms per unit cell in a crystal and the distance between the equivalent points that define the unit cell. Refinements on this technique led to new ways to determine density, independent of traditional mass measurements (X-ray crystal density or XRCD). It was not until 1965 that more precise measurements of atomic distances were possible which provided a new way of counting the atoms in a crystal (21). In the 1970s, scientists were able to make use of these new developments to determine Avogadro's number using "near" perfect crystals of silicon (22). It was these breakthroughs in XRCD that ultimately led to our current definition of the mole (23, 24).

In 1971, the 14th CGPM adopted the mole as a base unit in the International System of Units (SI) by defining it as follows (25):

> The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12.
>
> When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

Chemists have a unique challenge to measure the mass of the very small atom. To do this, there needs to be a relationship between the very small atom and the macroscopic or a weighable sample of an element. This led to a direct link between mass and the mole. The atomic mass unit, defined as 1/12 the mass of a carbon-12 atom, is very close to the mass of one proton (1.00728 amu) or neutron (1.00866 amu). The amu is related to the mass of an atom by 1 amu = $(1/6.022\times10^{23})$ g or one gram divided by Avogadro's number. This is an incredibly useful relationship which allows chemists to convert between the measurable unit of the gram and the number of atoms or molecules, a topic taught to every beginning student of chemistry (26-28).

When the international metrology community decided to redefine the kilogram due to the drift in mass of the IPK relative to the official copies and redefine the kilogram in relation to universal constants, this required a redefinition of the mole as well (3, 29). A fixed numerical value of N_A was the next step in a revision of the SI. The International Avogadro Coordination (IAC) began work in 2004 as a collaboration between several countries to redefine the mole. Several reports were published in *Metrologia* in 2011 (30), and at the 24th CGPM in 2011 the goals were clearly outlined in resolution 1 (31):

> •…that of the seven base units of the SI, only the kilogram is still defined in terms of a material artefact, namely, the international prototype of the kilogram (1st meeting of the CGPM, 1889, 3rd meeting of the CGPM, 1901), and that the definitions of the ampere, mole and candela depend on the kilogram,
>
> •that although the international prototype has served science and technology well since it was sanctioned by the CGPM at its 1st meeting in 1889, it has a number of important limitations, one of the most significant being that its mass is not explicitly linked to an invariant of nature and in consequence its long-term stability is not assured,
>
> •that the CGPM at its 21st meeting in 1999 adopted Resolution 7 in which it recommended that "national laboratories continue their efforts to refine experiments that link the unit of mass to fundamental or atomic constants with a view to a future redefinition of the kilogram,"
>
> •that many advances have been made in recent years in relating the mass of the international prototype to the Planck constant, *h*, by methods which include watt balances and measurements of the mass of a silicon atom, …
>
> •that it is also possible to redefine the mole so that it is linked to an exact numerical value of the Avogadro constant N_A, and is thus no longer dependent on the definition of the kilogram even when the kilogram is defined so that it is linked to an exact numerical value of *h*, thereby emphasizing the distinction between amount of substance and mass,
>
> •that the uncertainties of the values of many other important fundamental constants and energy conversion factors would be eliminated or greatly reduced if *h*, *e*, *k* and N_A had exact numerical values when expressed in SI units,
>
> •that the General Conference, at its 23rd meeting in 2007, adopted Resolution 12 in which it outlined the work that should be carried out by the NMIs, the BIPM and the International Committee for Weights and Measures (CIPM) together with its Consultative Committees (CCs) so that new definitions of the kilogram, ampere, kelvin, and mole in terms of fundamental constants could be adopted…

At the time of the 2011 conference, work had already begun on the two possible techniques to link the kilogram to the Planck constant. The Kibble balance (formerly known as a watt balance), which ultimately had more influence on the determination of the Planck constant (and kilogram), works like a scale by counteracting a 1 kg reference mass against the electromagnetic force required to hold up that reference (32). The Planck constant is proportional to the energy needed to balance the

mass. The Planck constant was found to be 6.62607015 × 10^{-34} Js by two independent laboratories (33).

The other method was based on earlier XRCD studies. These studies made it possible to precisely define Avogadro's constant. The challenge was to create pure enough silicon spheres to reduce uncertainty. There are three stable isotopes of silicon in nature: silicon-28, silicon-29 and silicon-30. Silicon-28 is the most abundant (about 92%). A German-Russian collaboration resulted in enriched silicon-28 created by a centrifugal cascade process which raised the purity of silicon-28 to 99.999% (34). Further breakthroughs came as a result of improvements in x-ray diffraction-interferometry methods and the development of mass spectrometry that used a plasma source for ionizing the sample. National metrology institutes around the world experimented with the enriched silicon-28 samples to see who could come up with the best way to measure the samples. Each scientific team created precise silicon-28 enriched spheres and measured their volumes with interferometry. Then the proportion of silicon isotopes was determined by mass spectrometry. Once the sphere volume was precisely determined and the composition of the crystal lattice known, scientists calculated Avogadro's constant (35).

In anticipation of the redefinition of the mole, The International Union of Pure and Applied Chemistry (IUPAC) in consultation with member organizations published a recommendation on the redefinition of the mole (36). As the definition of the mole was finalized in anticipation of the 2018 CGPM meeting, representatives from the IUPAC were able to influence the redefinition (37, 38).

In November of 2018, representatives from 60 countries gathered in Versailles, France to vote on redefining the mole as follows (14, 39):

> The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly 6.02214076 × 10^{23} elementary entities.
>
> This number is the fixed numerical value of the Avogadro constant, N_A, when expressed in the unit mol^{-1} and is called the Avogadro number.
>
> The amount of substance, symbol n, of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles.

The significance of this change is that the mole is no longer dependent on the definition of the kilogram; rather it is based on a specified number of elementary entities (atoms or molecules). From a pedagogy perspective, the *new* definition of the mole is closer to the way many chemistry teachers, students and textbooks understand the mole when compared to the previous definition which linked the mole to the elementary entities in 0.0120 kg of carbon-12. The new definition also recognizes the Avogadro number, the term more commonly used by chemists (37).

Looking forward, little will change in the way most experiments are planned and carried out (40). With the re-defining of the kilogram, the time was right for an independent definition of the mole. Horst Bettin, a chemist at the Physikalisch-Technische Bundesanstalt (PTB), Germany's national institute for weights and measures, summarizes it as follows (41),

> [the mole is] not a mass, it's a number.
>
> …the good thing in science is that scientists work together all over the world. That's why we reached this uncertainty [small tolerance] and can redefine [the mole].

The vast scale of the collaboration, the teams of scientists working together and the general agreement among metrologists seems to have realized the slogan of the originators of the metric system (4), *"A tous les temps, a tous les peoples (For all times for all peoples.)"*

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MOLECULES WITH FLUXIONAL STRUCTURE: AN INITIAL MOMENT IN THEIR CONCEPTION

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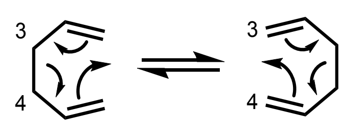
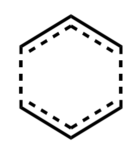
The structural theory of Kekulé (1), Couper (2) and Butlerow (3), marked the beginning of present day organic chemistry. It postulated that the individual atoms in a molecule are bonded with one another in a definite connectivity and that this connectivity defines the identity (i.e., structure) of a given compound composed of these molecules. This theory explained why different compounds with the same atomic composition exist (isomeric compounds) and how many different isomers are possible for a given composition. In order to convert one isomer of a given composition into another isomer, bonds between certain atoms have to be broken in the original isomer, and reconnected in a different fashion to reach the other isomer. This defines the bond changes that have to be accomplished in an isomerization reaction converting the structure of the initial compound into that of the product compound. Nothing is said at this stage about the number of steps and kinds of reagents necessary to effect this transformation. At least, it allows for a one-step intramolecular transformation without external reagents, simply triggered by supply of thermal or photochemical energy. Such processes are called *valence-isomerizations*, for which numerous examples are known (4). One could project a valence isomerization in which the structure of the initial and the final isomer are identical, a reaction with no net chemical transformation, i.e. a valence isomerization in which the breaking and forming bonds are related to one another by some symmetry element. In such a process the bonding situation between individual atoms is altered, while the overall bond pattern between all atoms is maintained. A representative example of such a process would be the Cope rearrangement (5) of 1,5-hexadiene (**1**):



1



1'

Provided this reaction is an intramolecular—not a dissociation-recombination—process, this constitutes a *degenerate* valence isomerization, in as much as the breaking and forming bonds are symmetry related in the transition state **1′**. The Cope rearrangement of 1,5-hexadiene was observed to occur at >200°C; the fate of individual atoms was demonstrated by tagging the 3- and 4-positions with deuterium (6).

Yet, there was a further extension regarding degenerate valence isomerizations lying dormant: What if such a degenerate valence isomerization were to occur at or below room temperature? What would this imply for our concrete notion of "structure of a compound" as defined by a distinct connectivity of ***individual*** atoms in a molecule? Whenever a degenerate valence isomerization in a molecule is occurring with an appreciable rate, its structure would be fluxional, while its structural identity is conserved. This would constitute a case at the limits of structural theory, as holds for the classical valence bond description of benzene. Even more fascinating and important, such molecules with fluxional structures would be at the transition region between molecules with traditional

bonding and those with delocalized bonding! It is these insights that mark an important step in the conceptual development of organic chemistry and justify the question, when, where, and by whom was this intellectual process initiated? Was it a parallel discovery at several independent places, or did it occur in a flash of genius, a single *historic moment*, at a distinct site?

A Historic Moment

A “moment”—as used in this essay—is defined as an assembly of one or more persons, one or more objects in a defined location and time. That means a situation, reduced to the essentials like a stage setting in a play. Most moments are inconsequential, as driving through an intersection past a green light. Some moments are consequential, as driving through an intersection past a red light and hitting another car. Consequences that may originate from this moment are, e.g., damage to either car that will have to be repaired, injuries to the people involved that need extended medical treatment, a court case eventually leading to a prison sentence, loss of employment because of the latter, and so on. Some moments cause a major sequence of other moments, a chain of effects that may ramify, much like an avalanche. At some point later people may ask, where, when, and why did all this start? This looking back in time brings in the “historic” element. Identifying the moment at the root of a sequence of consequential moments then defines it as the (or one) historic moment of the development. It is only in hindsight that a specific consequential moment may acquire the attribute “historic,” and, the attribute

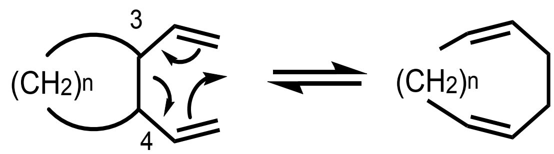
***Figure 1**. William von E. Doering (left) and Emanuel Vogel at Vogel’s home, Cologne, ca. 2000. Photograph courtesy Mrs. E. Vogel.*

“historic moment” should always be connected with a distinct sequence of events, a distinct development.

Molecules with Fluxional Structure

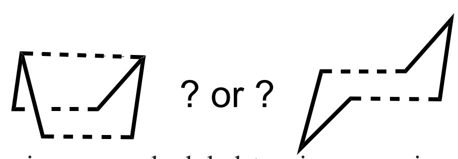
In hindsight, it appears probable that the phenomenon of molecules with fluxional structure would be discovered when studying variations of the Cope rearrangement. In the early 1960s there were two major players studying aspects of the Cope-rearrangement: Priv.Doz. Dr. Emanuel Vogel in Karlsruhe, Germany, and Prof. W. von E. Doering at Yale University in New Haven, Connecticut, USA (Figure 1).

Vogel was studying the influence of ring-strain at the C3-C4-bond on the facility of the Cope rearrangement, with n = 1-3 (7).



Doering was studying the transition state conformation of the Cope-rearrangement (8), probing, whether a six-center boat-like arrangement or a four-center chair-like arrangement is favored.

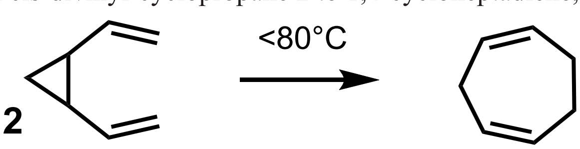
via



When Doering was scheduled to give a seminar speech on the “Mechanism of the Cope Rearrangement” in Heidelberg on April 25 (see (9, 10) and Figure 2), no results from these studies had been published beyond a three-sentence statement in a 1960 review by Vogel (11) on small carbon cycles.

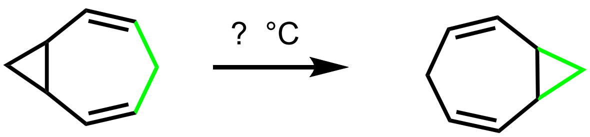
Vogel came up from nearby Karlsruhe to attend. Doering’s lecture focused on the studies on the transition state of the Cope-rearrangement. After the lecture had finished a handful of people (I was one of them) flocked together with Doering at the blackboard. After some other topics had been discussed, Vogel drew out at the blackboard his observations on the rearrangement of cis-divinyl-cyclopropane **2** to 1,4-cycloheptadiene,

2



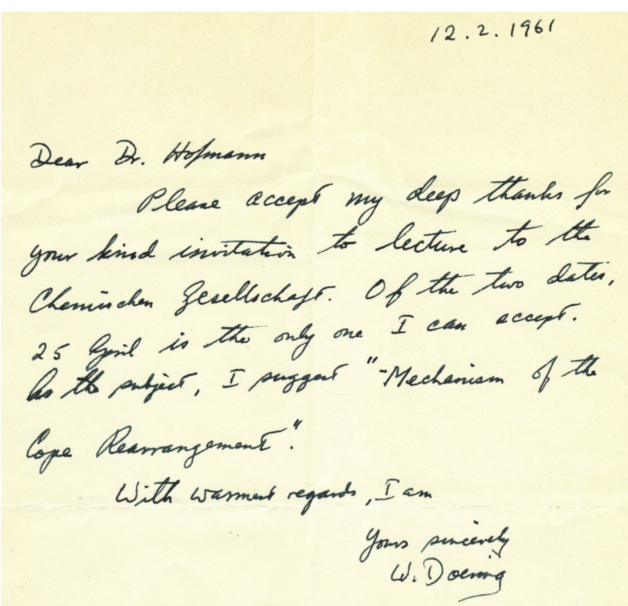
demonstrating the major effect the release of ring-strain

had on the rate of the Cope rearrangement. The discussion went to the entropic penalty caused by confining the dangling vinyl groups of **2** in the transition state. Upon which Vogel suggested to incorporate them into an additional cycle and supplemented his scheme with colored chalk:



3

Before Vogel could finish to put all the lines on the blackboard, Doering remarked "Hey, that's gonna be degenerate!" Most of the people present will have realized that when the rearrangement of **2** occurs well below 80°C—it later has been shown to occur at room temperature with a half-life of a few minutes (12)—molecules such as homotropilidene (**3)** would be fluxional at ambient temperature. The discussion ended shortly thereafter, and Doering, Vogel, and others adjourned for dinner. I do not know whether Vogel and Doering followed up on the discussion of a degenerate Cope rearrangement during the dinner. Any such discussion would however have been contingent upon the aftermath of Doering's lecture on April 25 in Heidelberg, which thus marked the birth of the concept of degenerate rearrangements on the way to molecules with fluxional structures.



12.2.1961

Dear Dr. Hofmann

Please accept my deep thanks for your kind invitation to lecture to the Chemischen Gesellschaft. Of the two dates, 25 April is the only one I can accept. As the subject, I suggest "Mechanism of the Cope Rearrangement".

With warmest regards, I am

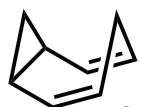
Yours sincerely

W. Doering

Figure 2. *Letter by W. v. E. Doering to Prof. U. Hofmann, the then Chairman of the Chemische Gesellschaft zu Heidelberg. Courtesy of Prof. G. Helmchen, Heidelberg 26.10.2021.*

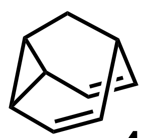
The Consequences

Once the significance of homotropilidene **3** had been recognized, its synthesis was right away undertaken and achieved by Doering and Roth (9). The NMR-spectrum showed at 20°C a coalescence of the vinylic proton signals and a coalescence of the remaining proton signals, thus proving the fluxional behavior. Does this synthesis, hence, mark another historic moment? Moment, yes, but historic? The attribute "historic" has to be weighted by the number and significance of the consequences. The synthesis and measurements of compound **3** were rather a point-contribution that marked a confirmation of a hypothesis, which was born in the April 25 historic moment. The latter had much farther-reaching consequences, as we will see, than just leading to a confirmation of its underlying hypothesis.



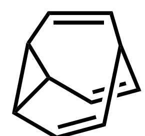
3

Homotropilidene



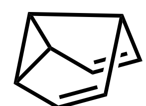
4

Barbaralane



5

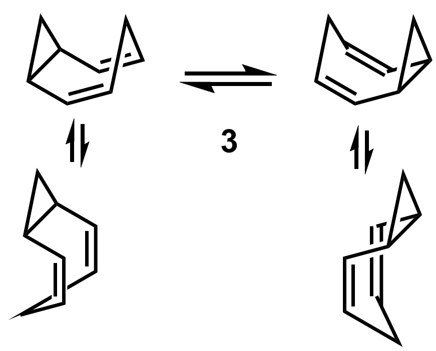
Bullvalene



6

Semibullvalene

The April 25 flash of genius led to a cascade of consequences, in which the conception and synthesis of compound **3** constituted only the first link. It was recognized that the resting state of compound **3** is a *trans*-folded conformation, which has to convert to the *cis*-folded conformation to allow the degenerate Cope rearrangement. Hence, bridging bow and stern of **3** would fix the *cis*-folded arrangement and should accelerate the Cope-rearrangement even further.



cis-folded

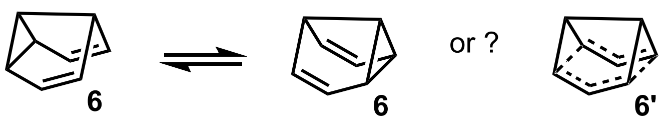
trans-folded

Accordingly, the bridged homotropilidene **4** dubbed barbaralane and derivatives thereof were envisaged and synthesized (13). Indeed compound **4** underwent an exceedingly fast degenerate rearrangement at 0°C (14)—a significant advance to generate molecules subject to rapidly degenerate rearrangement.

Another extension was initiated (first conceptually by Doering and Roth (9)) by bridging the bow and stern positions in **3** by a 1,2-ethenylidene bridge to result in compound **5**. The famous "bullvalene" **5** should be fully fluxional exchanging the positions of every C-H unit in its structure by degenerate Cope rearrangement. In due course, bullvalene was synthesized, first by G.Schröder (15), and subsequently by several differing routes later (14, 16). As anticipated, the ^{1}H-NMR spectrum of **5** is temperature dependent, showing only a single sharp C-H signal at 100°C (15).

Comparing the bridged homotropilidenes **4** and **5,** compound **4** with a one-carbon bridge rearranged substantially faster than compound **5** and related structures with a two-carbon bridge (14). This led one to expect, that compound **6**, semibullvalene might rearrange even faster.

When semibullvalene **6** was obtained by H. E. Zimmerman and G. L. Grunewald in 1965 (17), its degenerate rearrangement could not be frozen out even at –110°C. This led Zimmerman to speculate, that **6** might have or



come close to having a fully delocalized homoaromatic ground state **6′**.

A decade later, the free energy of activation for the isomerization of **6** could be determined to $\Delta^{\ddagger}G° = 5.5$ kcal/mol (18), validating Zimmerman's conclusion, that compound **6** is fluxional, but not delocalized (**6′**). Yet as R. V. Williams puts it (19), "It is generally recognized that semibullvalene (**6**) is the species most closely approaching the holy grail of neutral homoaromaticity" (20). Cf. **6′** with a delocalized six-electron system.

Thus semibullvalene (**6**) turned into a starting point of still ongoing worldwide research activities (19) to reach a delocalized derivative of **6′** by adding substituents or annelating rings to semibullvalene.

Conclusions

The aftermath of Doering's lecture at April 25, 1961, in the lecture hall of the old chemistry building of the University of Heidelberg in Akademiestrasse 5 in Heidelberg was not just any moment in chemistry. The consequences and sequence of consequences of this moment led to research activities that continue even today, 60 years later. This moment in Heidelberg can now be assigned to likely (21) be the key "historic moment for the development of molecules with fluxional structure."

The story of molecules with fluxional structure has been told before (22). Yet, every time a story is told, different details are revealed and highlighted, as holds for the present essay.

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20. While aromaticity refers to cyclic systems in which each ring atom contributes one p-orbital to the cyclic conjugation, **homoaromaticity** likewise refers to cyclic systems in which each ring atom *except one* contributes one p-orbital to the cyclic conjugation. Thus, cyclic conjugation has to bridge a one-atom gap. Bis-homoaromatic would refer to rings with two such bridging situations.
21. One may be tempted to consider an alternate scenario, that Doering had conceived homotropilidene (**3**) *and* had started working towards it *prior to* April 25, 1961. In this case, however, Doering's reaction to the disclosure of Vogel at the blackboard would probably have been a different one.
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About the Author

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Bite-sized Pieces of History

Every issue of the *Bulletin* contains short items, mainly announcements, in spaces like this, at the end of articles. It has been suggested to me that such spaces could also be used for short items of historical interest. I would welcome such short pieces to be collected and run as space permits. Please send such items of approximately 200-300 words to the Editor at giunta@lemoyne.edu under the subject heading "bite-sized history." Pieces will be subject to editing. Authors will be credited and notified.

—the Editor

HIST CENTENNIAL MEMORIES

AARON JOHN IHDE (1909-2000)

Gretchen Ihde Serrie and James J. Bohning; Edited by Carmen J. Giunta, Le Moyne College, Syracuse, NY, USA, giuntacj@gmail.com

Introduction

As promised in the HIST Centennial special issue of this journal, the *Bulletin* is running centennial features in each of its 2022 numbers (1). That Centennial issue included several articles that discussed chemist historians and historians of chemistry. This feature focuses on one of the key figures from HIST's first hundred years who stood firmly in both of those professional camps, Aaron J. Ihde (Figure 1). It highlights aspects of his personal and professional lives using materials graciously supplied by his daughter, Gretchen Ihde Serrie and others previously published by HIST. The spotlight begins with a biographical sketch prepared by long-time HIST historian James J. Bohning for the Division's collection of biographies of Dexter Award winners (2). After reviewing Ihde's career, this feature concludes with personal reminiscences excerpted from the eulogy prepared by his daughter for his memorial service in 2000 (3).

Ihde was no stranger to the *Bulletin*, despite his having retired before the journal was founded. He was a frequent contributor to its early numbers, including a series of articles on winners of the Division's Dexter Award (4). Ihde was on the cover of the *Bulletin* shortly after his death. Between the covers of that issue were several articles about him by HIST colleagues and former students (5) as well as a final article by him (6).

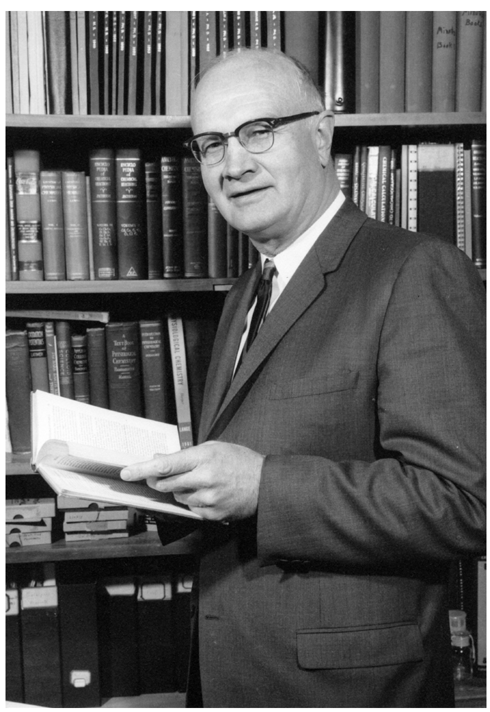

***Figure 1**. Aaron J. Ihde in his element (i.e., among books) in the middle 1960s. (Courtesy of Gretchen Ihde Serrie and the University of Wisconsin archives.)*

Biographical (2)

Aaron John Ihde was born on December 31, 1909, and raised on a dairy farm near Neenah, Wisconsin. His parents were the children of immigrants (7); they had little formal education, but they treasured books and learning. Aaron was only the fourth of his one-room country "K through 8" school to go on to high school. His parents realized his lack of interest in farming and supported their son to attend the University of Wisconsin in Madison. He graduated in 1931 from the university's "Chemistry Course" and accepted a job as the staff chemist at the Blue Valley Creamery Company in Chicago, Illinois (later acquired by Beatrice Foods), where he did

research and development on food products. It was at this time that he developed a deep interest in the history of food controls.

In early 1938 he returned to the University of Wisconsin in Madison where he majored in food chemistry (under Henry Schuette) and minored in biochemistry (under Harry Steenbock), earning his doctorate in 1941. It was Schuette who furthered his latent interests in the history of chemistry. After one year of teaching in the chemistry department at Butler University, Indianapolis, Indiana, he returned to Madison for a one-year instructorship in the chemistry department. Following two renewals of this appointment, in 1945 he was hired on the tenure track and carried a heavy teaching load in the freshman chemistry program during and after the war years. In the summer of 1946, he revived a dormant course in the history of chemistry previously taught by Louis Kahlenberg (until his retirement in 1940). Ihde's interest in the history of science was further recognized in 1947 when he was invited to teach the first science course, "The Physical Universe," of a two-year sequence of general studies of an interdisciplinary nature. Ihde's course, which drew material from chemistry, physics, and astronomy, sought to show the nature of science and the growth of scientific ideas through the historic debates associated with planetary systems, atomic and molecular theory, and cosmic concepts. He continued to teach the course until his retirement in 1980; more than 7,000 students took this course under his leadership. By 1949, Ihde had placed the history of science at the center of the new Integrated Liberal Studies Program at the University of Wisconsin.

Ihde's thrust toward history of science was accelerated by three parallel developments: 1) the creation of a major program in the history of science at Wisconsin—started in 1941 by Henry Guerlac and continued after the war by R. Stauffer and Marshall Clagett, with ancillary history programs in pharmacy, from Georg Urdang and medicine from Erwin Ackerknecht; 2) the university's purchase of Denis Duveen's book collection—supplementing the Thordarson Collection (1945, science and technology) and the later purchase of two collections of Hugh Sinclair (1957, Boyle and Priestley) and William A. Cole (1978, rich in revised editions and translations of eighteenth- and nineteenth-century European treatises); and 3) a year spent at Harvard University in 1951-52 as a Carnegie Intern in General Education, working with James B. Conant, Leonard Nash, and Thomas Kuhn in teaching Conant's Case History course in science. That year also permitted him to become associated with George Sarton, I. B. Cohen, and Gerald Holton in the history of science program they were developing at Harvard. In 1957, the University of Wisconsin's History of Science Department welcomed Ihde officially to its ranks. Ihde's research and publications transformed the field of the history of chemistry. The intellectual fruits of six decades at Wisconsin as a student, as a faculty member, and as professor emeritus occupy seven bound volumes in the stacks of the Memorial Library and consist of 342 items including a posthumous paper published in the *Bulletin for the History of Chemistry* [(6)]. He made the University of Wisconsin the premier center for the study of the history of chemistry especially after he was joined on the faculty by his first Ph.D. student Robert Siegfried. Over the years, Aaron supervised 21 Ph.D.s in history of science, as well as a number of masters students and post-doctoral fellows. His best known books are *The Development of Modern Chemistry* (1964) and his volume of *Selected Readings in the History of Chemistry* (1965), culled from the *Journal of Chemical Education* and co-edited with the journal's editor William Kieffer. *The Development of Modern Chemistry*, the standard textbook in the field, included the history of chemical technology, biochemistry, agricultural chemistry, and chemical physics, extending coverage to the first half of the twentieth century. He wrote broadly and widely about Paracelsus and Boyle, on classic nineteenth-century European scientists such as Avogadro, Faraday, Bunsen, and Baeyer, on the development of chemistry in the United States, and on the history of the pure food law.

Ihde was an advocate of progressive causes, especially the social responsibilities of scientists, and the purity and safety of drugs. From 1955 to 1968 he was a member of the Wisconsin Food Standards Advisory Committee and served as its chair for two years. In 1958 he was offered the position of scientific director of Consumers Union, but declined a position that would have doubled his salary because he loved his work as a scholar and teacher. In the early 1960s Aaron Ihde and other University of Wisconsin professors, including Grant Cottam, James Crow, Arthur Hasler, Hugh Iltis, Karl Schmidt, and Van Potter, advocated public and scholarly discussion of Rachel Carson's *Silent Spring* and the impact of pesticides on the environment. As a result, they were accused of spreading false and misleading information and some questioned their competence and their qualifications to speak to the public about pesticides.

Ihde was admired and respected by students and colleagues. All his dealings with students were models of organization, dignity, and respect for scholarly inquiry.

He was generous in making all his books and resources available to any visitor to his office. He promoted and enjoyed contacts with alumni and former students. He was the long-time editor of the *Badger Chemist*. His interest in the history of the University of Wisconsin Department

Figure 2. *The Ihde family in 1948. Left to right: Olive and Aaron (rear), Gretchen and John (front). (Courtesy of Gretchen Ihde Serrie.)*

of Chemistry resulted in the publication in 1990 of his last book: *Chemistry, As Viewed from Bascom's Hill: A History of the Chemistry Department at the University of Wisconsin in Madison*.

Ihde received the Dexter Award in 1968 and the University of Wisconsin's Chancellor's Award for Distinguished Teaching in 1978. He served as president of the Wisconsin Academy of Science, Arts, and Letters, chair of the ACS Wisconsin Section, and chair of the ACS History of Chemistry Division (1962-1964). He was elected fellow of the American Association for the Advancement of Science. He remained active in retirement and devoted himself to reading, writing, family visits, and volunteer work in the Arboretum, removing invasive honeysuckle and buckthorn thickets from the Lost City Forest section of the Arboretum; over the years he single-handedly restored a large wildflower meadow. He spent his final eighteen months with his daughter Gretchen and her family in Sarasota, Florida, where he began to show symptoms of Alzheimer's disease. He is survived by his two children and their families. [His wife, Olive Jane Ihde, née Tipler, had died in 1988. Figure 2 shows the Ihde family.] Aaron Ihde died on February 23, 2000, in Sarasota, Florida.

Family Remembrances (3)

[Figure 3 shows Ihde with his daughter, Gretchen, when he received his doctorate in 1941. Figure 4 shows the same two in a scenic spot in 1993.]

Figure 3. *Aaron Ihde, about to receive his Ph.D. in 1941, with his daughter Gretchen. (Courtesy of Gretchen Ihde Serrie.)*

So many of Dad's, and Mom's, students, colleagues, and friends have written our family since his death. The word most often used to describe him has been "gentleman." One person called him a "gentleman and a scholar," which made me chuckle, because we used to tease people by saying, "You're a gentlemen and a scholar." But Dad was a proud scholar, and he was a gentleman.

One of the writers didn't have enough room at the end of the line for gentleman and divided it. The separate words almost pulsated at the end and beginning of two lines, becoming a "gentle man." And, indeed, my father was a gentle man, he was the gentlest of men,

For years, for some reason I can't explain, one memory of my father has always stood stark in my mind, I was not more than eight or ten, my brother John, four or six. We were travelling back to Madison after a weekend visiting our grandparents, a ritual my parents, both only children, devotedly repeated every two weeks. It was a dreary November day, cold and grey. Our car hit a pheasant, which dragged itself into the woods. Dad stopped the car, leaving Mom, John, and me, and traipsed into the woods, searching for the pheasant for half an hour. He did not find the bird and was tormented by the incident the rest of the way home. If he had found it, he would have taken it home and tried to nurse it back to health.

…

"Gentle" is the first adjective that describes him. Another word does as well, a very old fashioned one, "bashful." Dad was an incredibly shy person. Actually, Ihde (pronounced Ide) was not his real last name. He was born Aaron Ihde (pronounced Ede). As a freshman at the University of Wisconsin, he never had the courage to correct his teachers when they mispronounced his name "Aaron Ihde [Ide]." When he returned for graduate study, as he left for his first day of classes Mom told him, "Now, Aaron, you have to inform your professors you are Aaron Ihde [Ede]." He came home that evening, hanging his head, and said, "Olive, I just can't do it." So they led two lives, Aaron and Olive Ihde [Ede] in Neenah, Wisconsin, and Aaron and Olive lhde [Ide] in Madison, with relatives muttering about the airs Olive and Aaron had put on since arriving in the big city.

Mom told me that in high school Dad was so shy that whenever a girl spoke to him he would turn beet red. A favorite Neenah High School pastime was to have a girl seek out Aaron and walk down the hallway with him while her friends watched him blush to the roots of his white-blond hair.

…

My father was a temperate man: little wine, no cigarettes, my mother the only woman in his life. However, he did have one addiction, from which no twelve-step recovery program could ever have cured him: it was books. He never met a book he didn't love. If books were hard liquor, he could have been the father in *Angela's Ashes*. There was never a room or hallway or attic in any house we owned that didn't have bookcases. The year we spent in Boston, when Dad was a Carnegie fellow at Harvard, he would come home almost tipsy with the joy of having spent the day imbibing in the used book stores of Cambridge. I remember him actually throwing his hat up the stairs one night as he arrived with a big box of books he had purchased, to see if he was still welcome home after this latest binge.

He rarely read fiction—always serious material, always underlining and making marginal notes, even, for the past two years, in many of the books in my patient husband's library. When Dad finally had to leave our home to live in the Westminster Asbury memory unit, for several weeks he carried about with him his chosen reading material—*The Food Crisis in Pre-History*. The saddest loss in his last year was his ability to read.

…

Figure 4*. Gretchen Ihde Serrie and Aaron Ihde in Northern Wisconsin, 1993. (Courtesy of Gretchen Ihde Serrie.)*

I decided to try to sum up the life lessons I learned from my parents. They are these.

1) Have a social conscience. This was usually preceded by, "Gretchen, will you ever develop a social conscience?" The words "social conscience" are not heard frequently nowadays, but they meant striving, to the best of your ability, to take good care of the individuals in your life, of those in the community in which you lived, and of the larger community which is this earth and all of its resources.

2) Desserts are good for you. Have desserts for breakfast, lunch, and dinner and as a snack before you go to bed. If you are grandchildren, have even more desserts. If you are grandparents, facilitate this.

3) Vote for the Democrat. Mom cast her very first vote for Herbert Hoover, an act Dad delighted in teasing her about. My grandma, a liberated women who worked in the fields beside her husband, pitching hay and driving horses, refused to vote, feeling that was not a women's

place. But in 1932 my grandpa popped her into the car and said, "We've got to vote for Franklin Roosevelt And I'm taking you with me." That was the beginning of a fierce and unwavering family allegiance to the Democratic Party, although my Dad's Puritanic soul was sorely tested by Bill Clinton.

The corollary to "Vote for the Democrat" is: Liberal is not a bad word. Dad was a proud and unabashed liberal, be it in politics or in education, as in "Integrated Liberal Studies." Dad also never forgave *Time Magazine* for calling Adlai Stevenson an "egghead," punishing *Time* by cancelling his subscription and depriving himself of what for years had been among his favorite recreational reading material.

4) Books are good. More books are better.

5) Co-ops are good. Buy your gas at a co-op gas station, even if you have to drive 100 extra miles out of the way to get to it. And keep all of your money in a Credit Union.

6) Historians never throw anything away. This tradition is carried on by his grand-daughter Jennie. Amongst the incredible UW memorabilia we found on moving day from Dad's Chemistry Department office were glass shards from the explosion in Sterling Hall during that period in the 60's which so traumatized and demoralized Dad's generation of professors.

7) Let your children follow their dreams. Dad didn't discover until the middle of his career that what he really wanted to be when he grew up was a historian of chemistry. His expectations of us were only that whatever we did, at whatever period of our life, we would do it responsibly and to the very best of our abilities.

8) Sports are an important part of life and not just for guys. He told me, "I don't want to have a daughter who throws like a girl!" (not a very P.C. way to put it nowadays, but not bad for the forties) and taught me to throw a baseball just as well as the boys in the neighborhood. He was proud that his granddaughters participated in sports.

9) Fill your life with music. Our radio was tuned to WHA from the time I woke up until I went to bed. These two kids from central Wisconsin farms had exquisite taste in music.

10) Make the best of things. Our greatest and final test is how we leave this life, and my father got an A plus. He lost a great part of that marvelous mind and memory, yet retained what is most important, the ability to love. He told us he loved us from the time we were born until his very last hours in the hospital. He didn't love us because we'd received an honor, gotten an A on a test, won a basketball game, played a good concert, but just because we were his children, grandchildren, students, or friends. Kind of a precursor to Mr. Rogers, a 225 pound Mr. Rogers, he loved us all "just the way we were".

Lastly, and most important, I learned from my Dad, and my Mom, what a better place the world would be if each and every one of us were "gentle persons".

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7. His grandparents immigrated to the US in the 1850s from Mecklenburg, in the northeastern part of the current German nation state. Ihde grew up in a German-speaking home. (G. Ihde Serrie, personal communication.)

HIST CENTENNIAL MEMORIES

GEORGE KAUFFMAN: A PERSONAL REMINISCENCE

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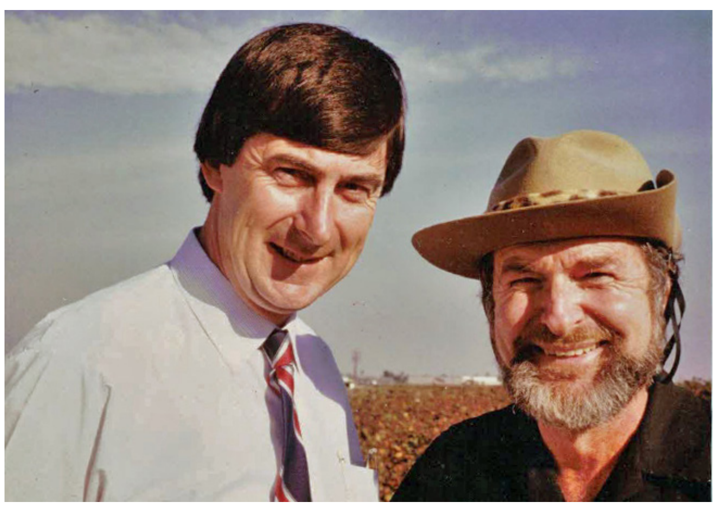
I was very interested to read Jeff Seeman's obituary-tribute to George Kauffman in the Fall 2022 *Bulletin* (*Bull. Hist. Chem.*, **2022**, *46*(2), 205-217). I got to know George because of a mutual interest in writing about chemistry, a meeting of minds that was triggered by my reading his "Alias J. J. Connington: the Life and Work of Alfred W. Stuart (1880-1947) Chemist and Novelist," (*J. Chem. Educ.*, **1983**, *60*(1), 38-40). I had included Connington/Stewart and his chemist Sir Clinton Driffield in my article "Dustcoats in Dustjackets" published by the Royal Australian Chemical Institute (*Chemistry in Australia*, **1982**, *49*, 162-165) and later by the Royal Society of Chemistry (*Chemistry in Britain*, **1983**, *19*, 565-569).



Ian Rae (left) and George Kauffman in the early 1980s

I wrote to George about our mutual interest, and he invited me to visit so we could talk more about it. I was able to accept his invitation in October of the following year, and the photograph shows us in the cotton field at California State University Fresno. I was envious of what I thought was his ability to visit Britain to research his piece, but he said it was all sourced from literature and with the help of excellent librarians at Fresno and in UK. He encouraged me to do the same, a key piece of advice as I moved away from the laboratory. Of course the advent of the internet has made long-distance research even more possible but I still rely on librarians for expert assistance.

George and I kept in touch by mail, and we soon found another coincidence. George was collaborating in the translation of a biography of the Russian chemist and composer Alexander Borodin (*Aleksandr Porfir'evich Borodin. A Chemist's Biography*, by N. A. Figurovskii and Yu. I. Solov'ev, translated by Charlene Steinberg and George B. Kauffman, Springer, 1988), while I had been working on a study of Borodin's published chemistry ("The Research in Organic Chemistry of Aleksandr Borodin (1833-1887)," *Ambix*, **1989**, *36*, 122-137). We joined forces with Yuri Solov'ev to produce a "popular" version for *Chemical and Engineering News* and were delighted when it was the cover story for the magazine when it was published (G. B.

Kauffman, I. D. Rae, Yu. I. Solov'ev and C. Steinberg, "Borodin, Composer and Chemist," *Chem. Eng. News*, **1987**, *65*(7), 28-38.).

This called for a celebration, so once again I stopped off at Fresno, where George and Laurie were generous hosts. I learned a lot about the Central Valley—not a place that draws many tourists from overseas—and George and I enjoyed a meal at a restaurant run by the Armenian community who made their own potent red wine. This being California, George and I enjoyed a hot tub—Laurie bought us a beer!—and I inspected George's schneckengarten where he was raising a crop of snails for the table.

Years later we teamed up again to write about the Czech chemist and composer Emil Votoček (G. B. Kauffman, F. Jursik and I. D. Rae, "Emil Votoček (1872-1950): A Tribute to the Czech Chemist-Composer-Lexicographer," *Journal of Chemical Education*, **1999**, *76*, 511-519).

I had an invitation to George's 80th birthday bash, but the best I could do was to phone in with a greeting. Nobody answered the phone and I found out later that they had all been in the backyard. If only I'd had his cell phone number … but then I wonder if George ever had a cell phone: it didn't seem like his style.

ICHC 2023 in Vilnius – Call for Papers

13 ICHC Vilnius – Lithuania 2023

The Working Party on History of Chemistry (WPHC) of the European Chemical Society (EuChemS) announced the first call for papers for the 13th International Conference on History of Chemistry (13ICHC). The meeting, intended to bring together historically interested chemists, chemistry educators and historians of chemistry from all over Europe and beyond, is scheduled for Vilnius, Lithuania, from Tuesday 23 May to Friday 26 May 2023. The conference will be hosted by Vilnius University (established in 1579), in the old city.

The conference will include scientific sessions, key-note lectures, a poster session, the WP business meeting, as well as social events such as excursions, receptions, and a conference dinner. Information about the city and about an excursion organized for Saturday 27 May 2023 can be found on the conference website, https://www.ichc2023vilnius.chgf.vu.lt.

The call for papers and for panel or session proposals has a deadline of 1 December 2022. The 13ICHC welcomes proposals on any topic on the history of chemistry, broadly understood, including historical works on molecular sciences, life sciences, industry, technology, and education. We will also welcome papers on the teaching of history of chemistry, in order to reach out to the wider community and to students and young colleagues in particular.

All proposals must be in English, the language of the conference. Submitted abstracts and session proposals (max. 200 words) will be subject to review by an international Advisory Committee, that assists the Steering Organising Committee to ensure the quality of the conference program. Sessions should include about 3-5 papers, and no more than one session can be proposed by the same organizer. There is a limit of one paper per presenter (including the papers listed inside a panel or a session). All proposals must use the templates provided on the conference website, https://www.ichc2023vilnius.chgf.vu.lt/call-for-papers.

BOOK REVIEWS

Chemistry in 17th-Century New England, Gary Patterson, Springer, Cham, 2020, 94 pp, ISBN 9783030432607, $69.99 (paper), $58.90 (ebook).

Stemming from a symposium supported by the History of Chemistry Division of the ACS concerning the history of chemistry in America before the induction of the Society in 1876, this concise but dense work deals with the acts and deeds surrounding the southern New England-based alchemical *milieu* of John Winthrop Jr (1606-1676), monopolist, founding member of the Royal Society, third and fifth Governor of the Connecticut Colony.

Scholars who write on topics concerning the conceptualization of chemical knowledge usually take care to spend some time discussing the issue of the historical demarcation between alchemy and chemistry. This sort of categorization is not part of Patterson's purpose in this book. Some scholars will object to the author's approval of so much of Winthrop's conceptual, working and human framework and to his avoidance of those methodological constructs which have become a permanent fixture in the so-called "new historiography of alchemy." But more than one of those same scholars will have to admit that we can all learn from someone—a scientist, in this case—who writes like a fan rather than the umpteenth unconvincing epistemologist.

Fascinating as it is, the spread of European alchemy and chemistry in the New World is a subject that has rarely met with scholarly interest, and no major contribution was produced until 1994, the year of publication of the seminal work by William R. Newman, *Gehennical Fire: The Lives of George Starkey, an American Alchemist in the Scientific Revolution*. Since then, several other scholars have produced contributions to the history of alchemy in New England, focusing exclusively on the Boston area. Patterson's book, however, represents the second contribution dedicated to the topic but with a different geographical focus. In fact, it owes much to the only other monographic work dedicated to Winthrop, published in 2011 by the State Historian of Connecticut, Walter W. Woodward: *Prospero's America. John Winthrop, Jr., Alchemy, and the Creation of New England Culture (1606-1676).*

Of the eleven chapters constituting the book, the first and the last (pp 1-7, 91-94) are an introduction and general conclusions. Chapter 2 (pp 9-13) deals with the religious and philosophical thought of Winthrop. The author proves to be well aware of the hermeneutic shortcomings of the historiography preceding Newman's breakthrough, which mistakenly sought to identify alchemy exclusively as a branch of magical thought and, as such, incompatible with the colonists' Puritanism. The current state of research recognizes instead how alchemy proved to be consistent with Puritan values. As shown by Winthrop and his circle, Connecticut and Massachusetts Congregational Puritans broadly understood alchemy to be an intellectual and utilitarian endeavor but simultaneously offering the possibility for unmediated spiritual practices. Fostering propensities towards horizons of shared knowledge and common weal, Puritan alchemists hoped to achieve scientific advancements of both practical value and religious relevance. As for the supposed adherence of Winthrop's philosophical

thought to that of Francis Bacon (pp 12-13), although it is a suggestive hypothesis, it requires dedicated studies and cannot be accepted uncritically for a number of reasons. First is the mixed evaluation of alchemy espoused by Lord Verulam; second is his general aversion to the combination of natural philosophy and religious beliefs characterizing alchemical thought. On the other hand, as the author clearly shows, Winthrop fully understood the centrality of technological advancement for social purposes—constantly seeking the commercial stability and industrial independence of the territories under his political control—and generally endorsed the Baconian call for an empirically based "great instauration of knowledge." In Patterson's words: "John Winthrop, Jr., understood both the need for spiritual guidance and the constraint of public knowledge judged by groups of active researchers" (p. 12). Thus, for Winthrop, being a proto-industrialist in public and an alchemist in private did not represent a contradiction but a coherent balancing of his scientific, religious and social hopes and designs.

Chapter 3 (pp 15-22) presents a rapid overview of the situation of the Connecticut settlers upon Winthrop's arrival in the New World, while chapter 4 (pp 23-32) discusses his alchemical formation and accession to the Massachusetts Bay Company, with interesting insights on his passion for alchemical book collecting. Chapters 5 to 8 (pp 33-70) are undoubtedly the most compelling in the book, as they cover those aspects of Winthrop's work not dealt with or only hinted at in Woodward's contribution, from the foundation of the city of Agawam (today Ipswich, MA) to the implementation of industrial planning including the establishment of saltworks instrumental for the conservation of fish to be exported and the introduction of ironworks in the city of Braintree (MA). Related chemical processes and operations are reconstructed and described (offering the possibility for future in-depth research pertinent to archaeological chemistry) together with insights concerning their technological-industrial rendering. By the way, since these chapters are largely interested in topics concerning the exploitation of land and natural resources, maybe a wider examination of relations and knowledge exchanges between settlers and Native American people (i.e. Pequot and Mohegan nations) would have been advisable, especially since dedicated literature is vast and updated.

Chapters 9 and 10 (pp 71-89) respectively offer a reconstruction of Winthrop's alchemical circle with short biographies of prominent members (e.g., the young George Starkey) and a brief discussion concerning the teaching of medicine and elements of chemistry (especially iatrochemistry) at Harvard during the first decades of the institution's history.

Written in a swift and agile style, nearly narrative and at times (a bit too) apologetic for the story's main character, *Chemistry in 17th-Century New England* is a far cry from the way professional historians have been accustomed to conducting research in the history of science over the past fifty years or so. Nevertheless, in the most varied—sometimes even unorthodox—ways, it offers interesting food for thought, as well as delving into little-explored topics and pointing to new research possibilities.

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Technoscience in History: Prussia, 1750-1850, Ursula Klein, The MIT Press, Cambridge (MA)-London, 2020, 336 pp, 24 figs, ISBN 9780262539296, $40 (paper), $35.90 (ebook).

> Historians and philosophers of science have long treated the engineering and technological sciences as the natural sciences' poor relatives, and they have scarcely paid attention to the eighteenth-century sciences of mining, technical chemistry, mechanical engineering, civil engineering, and other "practical" or "useful sciences." "Science" was measured against the standard of "pure science" and epistemic values such as truth to nature, rationality, and objectivity. The historiography of science was thus framed by a concept of science that was only fully articulated by the middle of the nineteenth century and reached its height during the Cold War. Even today, long after the end of that conflict, historians and philosophers of science are rarely concerned with the engineering and technological sciences. The recent debate on "technoscience" also remains fixated on the newest application-oriented research projects at universities, while for the most part neglecting to make the obvious comparison to the tradition of engineering and technological sciences. (pp 3-4)

Despite this dynamic having been widely observed (and variously criticized) in the history of science since the early 1970s (1), only in recent years has Academia started to acknowledge how biased were those "ideological reasons" (p 241) that identified early modern and modern science as the triadic domain of natural philosophy, natural history and mixed mathematics, while diminishing (when not entirely ignoring) the role played by technical know-how and technological advancement. In this context, the work by Ursula Klein, among the most prolific scholars invested in the early modern and modern history of technology, represents a substantial step in the right direction.

The book takes off refuting the idea that the connection and commingling of science and technology called "technoscience" (after the definition popularized in 1987 by Bruno Latour's *Science in Action*) is a by-product of twentieth-century postmodernism, tracing back its roots in the mid-eighteenth-century concept of "useful science" (*nützliche Wissenschaft*). In this sense, the title chosen for the book has something of a provocative feel to it, since at the heart of the discussion is precisely the accurate historical reconstruction of that tradition of studies and research known as "useful science," which over time evolved, first becoming "technological science" during the nineteenth century and finally "technoscience" in its own right. The latter is thus framed as the product of a complex series of historical dynamics and not as an ex-novo creation of post-war western industrialization.

From a purely methodological point of view, such categorization principles are often criticized by scholars involved in history of science research centered in primary sources, as they automatically risk producing fallacious or at least anachronistic generalizations. The present book is an exception for at least two reasons. On the one hand, the categorization of "useful science" (and its evolutions) is modelled, as specified in the work's subtitle, on the single case study of the Kingdom of Prussia between the Seven Years' War (1756-63) and the period immediately preceding the Austro-Prussian War (1866). Such a case study could offer—as it actually seems—a useful locus of comparison for studies concerning other European powers (and their colonial domains) operating in the period under consideration. On the other hand, categorizations and related classifications used by the author, even if at times extremely broad, are based and derived from the primary sources employed and investigated, building on previous research of which the present book represents both updated reworking and further development (in particular *Nützliches Wissen: Die Erfindung der Technikwissenschaften*, Wallstein Verlag, Göttingen, 2016).

Now, what does the author mean when she speaks of "technoscience?" While not simply delimitating it within the boundaries of developmental reciprocity between experimental research and technical equipment or between the scientists' skills and their technical knowledge, Klein also recognizes the implausibility of generalizing the concept as enunciated by Latour, namely as the entanglement of science, technology and industry. Thus, once put in historical perspective, mid-eighteenth century "useful science"—including in a common epistemological model both natural-scientific and technological knowledge with related and progressive institutionalization of a scientific approach towards the resolution of problems essentially pertinent to technology—evolved into the nineteenth-century system of "technological sciences." These increasingly departed from the original state-oriented framework of "useful science," while becoming more and more relevant for private industry. "Technological sciences" also reached a codified institutional and educational regulation through the establishment of mandatory study courses, dedicated textbooks, handbooks, journals, review meetings and conferences, etc. Moreover, as a result of scientific specialization, once natural inquiry became an integral part of "useful science," it started forming the core of new, theoretical subdisciplines. The final step is represented by the further evolution into proper "technoscience," intended as

> interdependence and local convergence of technological and natural-scientific knowledge and inquiry in the framework of distinct institutions, such as military schools, engineering colleges, technical universities, modern research universities, and industrial research labs. (p 239)

Although the concept of "useful science" does not fall within a purely utilitarian application horizon, utilitarianism is undoubtedly one of its driving forces, especially in an increasingly preponderant manner since the shift towards "technological sciences." The genealogy of the relations between science and technology described and maintained by the author for the case of Prussia, in fact, illustrates the passage from the centrality of "useful science" (particularly with regard to mining, agriculture, forestry, saltworks, pharmacy and civil engineering) in statist projects with a social impact, towards forms of institutionalization of the "technological sciences" designed mainly to foster and incentivize progressively privatized forms of industrialization. In this regard, Klein's book fulfils another task. It offers a privileged starting point for whoever—within the still

narrow community of social historians (and philosophers) of technology—aims at investigating the relational reciprocity between the changes in the interactions of humans and nature described by technological advancement and the changes occurring in the corresponding societies, as originally hypothesized by Francis Bacon and later made famous with the dissemination of Marxist thought.

In the four parts into which the book is structured, the transformative and evolutionary dynamics of the relationship between science and technology in Prussia are investigated through the history of specific institutions, the professional figures working in them, and the personalities representing the scientific and politico-economical drive behind the changes and reforms at the heart of the discussion.

Part I (pp 19-80) identifies Prussian public administration environments as the cradle of the first projects aimed at the elaboration of industrial development policies. Starting from the analysis of the research and development programs (concerning forestry, agriculture, pharmaceutical chemistry and porcelain manufacture) presented in the Royal Prussian Academy of Sciences and other public institutions since the 1760s, Klein illustrates the substantial tendency toward the systematic recruitment, implemented by the state, of scholars, academics and craftsmen who contributed to the consolidation of the professional figure of the "technical expert" (*Sachkundiger* or *Sachverständiger*),

> a person who possessed extraordinary empirical and practical knowledge about a particular technical field that was, as a rule, at the margins of, or entirely outside, the sphere of regular artisanal professions subject to guild regulations (p 77)

This represents a particularly significant moment in Prussian history of technology as it indicates clear planning of generalized institutionalization in the relations between scientific knowledge and technical know-how aimed at research and development. Prior to this moment, such project organization is observed—foreign to whatever concept of industrialization—only in restricted environments (e.g. mid-to-late seventeenth-century academies like the Accademia del Cimento and the Royal Society), in individual disciplines (e.g., eighteenth-century French and Swedish Academic research on chemistry) or with individual researchers (in the cases of pharmaceutics and iatrochemistry especially from Paracelsus onwards).

Part II (pp 83-147) discusses what is described as the model of "useful science" in context through the paradigmatic example of the first educational institution intended for mining and geological research, the Saxon Mining Academy (*Bergakademie*), founded in 1765 in Freiberg. The modes of organization and teaching of "useful science" in this institution and their transmission to other branches of the fledgling public tech sector and private industry are also discussed, including interesting insights on individuals who tried to bridge the gap between the academic elitism of theoretical research and the perceived profanity of practical labor, such as Abraham Gottlob Werner, Carl Abraham Gerhard and Alexander von Humboldt, whose work as chief mining master (*Oberbergmeister*) in Prussian Franconia between 1792 and 1797 was already treated in great detail by Klein in previous work (*Humboldts Preußen: Wissenschaft und Technik im Aufbruch*, WBG, Darmstadt, 2015, pp 55-191).

Parts III and IV (pp 151-241) deal with the passage from "useful science" to 'technological science," focusing on the evolution of the relevant professional figures. As a consequence of the progressive specialization and successful institutionalization of "useful science," *Sachkundiger* and *Sachverständiger* gradually turned into *Techniker* and *Ingenieur* (cf. pp 221-222). Besides, the late-eighteenth century "scientific-technological expert," who in most cases was a public official—a minister, on several occasions—with a proper scientific educational background and profound technical knowledge, while keeping on staffing academies and both private and public educational institutions, ended up slipping through the net of state administration, transforming in a formidable asset for an industrial sector eminently devoted to liberalism, such as that of mid-nineteenth century Prussia (cf. pp 209-225).

The book ends with some thoughtful yet sharp evaluations of an epistemological nature, which will upset more than one philosopher of science while offering intriguing matter for reflection. In fact, although Klein argues that "if there was something like an epistemology of useful science, it was pragmatism," she also agrees with Friedrich Anton von Heinitz (one of the founders of the *Bergakademie*) affirming that "useful science" was based on a theoretical framework according to which the "reliability of knowledge" took priority over scientific "truths" (p 232). This implies that, besides giving knowledge a specific function in practice, "useful science" was, at least in part, self-conscious of the contingent and transient nature of its wealth of knowledge. And this was happening some one hundred years before philosophers of science began to implement concepts of contingentism

and conventionalism which, with the work of authors the likes of Ernst Mach, Émile Boutroux and Henri Poincaré (to name but a few among the most famous), would have forever changed the way we understand science and scientific research.

Thoroughly researched and coherently designed, *Technoscience in History* represents both a valuable contribution to the history of science and technology and a possible benchmark for future comparative studies dedicated to the relationships between scientific research, technological development, political agendas and related social impact. Furthermore, the author is to be credited with having succeeded in isolating the source-based hermeneutical device of "useful science" while avoiding the usual methodological controversies and abstractions that haunt the discourse of history of science.

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1. Cf., e.g., P. Rossi, *Philosophy, Technology, and the Arts in the Early Modern Era*, Harper & Row, New York-Evanston (IL)-London, 1970. E. T. Layton Jr, "Mirror-Image Twins: The Communities of Science and Technology in 19th-Century America," *Technology and Culture*, **1971**, *12*(4), 562-580. D. S. L. Cardwell, *Turning Points in Western Technology: A Study of Technology, Science and History*, Science History Publications, New York, 1974.

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150 Years of the Periodic Table: A Commemorative Symposium, Carmen J. Giunta, Vera V. Mainz, Gregory S. Girolami, Eds., Springer, 2021, 460 pp, ISBN 978-3-030-67909-5 (cloth, $149.99) or 978-3-030-67910-1 (ebook, $109).

This book presents a group of essays from the ACS Commemorative Symposium, celebrating the International Year of the Periodic table (IYPT), declared by UNESCO in 2019. This impressive book has clearly been carefully planned to include a variety of stories which are both entertaining and full of data available nowhere else. In my opinion, this is the best review of the Periodic Table of the Chemical Elements that has appeared. This collection describes both the historical and theoretical aspects of the Periodic Table, covering in extreme depth the many aspects of the evolution of the Table.

***Figure 1**. Logo of the International Year of the Periodic Table (www.iypt2019.org)*

Commonly in the literature there is one "author" of the Periodic Table—Dimitri Mendeleev—and this idea is reflected in the IYPT logo. However, as *150 Years of the Periodic Table* shows, there may actually be considered "multiple discoveries" leading up to the Periodic Table. In the words of Roald Hoffmann concerning another review of the elements, the history of chemical discoveries follows "lovely meandering paths, leading to an understanding of how chemistry really works" (1).

The book *150 Years of the Periodic Table* is divided into three sections: Mendeleev and his Predecessors, Discoveries of Elements, and Other Perspectives.

Mendeleev and His Predecessors

This section presents a history of events leading up to Mendeleev's publication in 1869. As chemistry progressed after Lavoisier's recognition of the "simple substances" in 1789, it became clear that the atomic weights might be a good method of organizing the elements ("Philosophy, Periodicity, and Predictions," by Ann Robinson). In her essay Robinson reviews the major steps in the evolution of the Periodic Table and introduces the distinction between elements and "simple substances," a question raised by chemists of the time when the nature of an "element" was not clear: Was an element an abstract concept or something physically "real"? The question was an important one to Mendeleev, who did not believe in atoms.

Attempts to correlate chemical behavior with atomic weights include Döbereiner's "triads" ("The Trouble with Triads," by William Jensen). Next, an essay on the "Telluric Screw" by Carmen Giunta describes a three-dimensional representation prepared by the French scientist Béguyer de Chancourtois to describe periodic behavior. Then the British scientists William Odling and John Newlands prepared tabular arrangement of the elements ("Periodicity in Britain" by Carmen Giunta, Vera Mainz, and Julianna Poole-Sawyer). Newlands' "Law of Octaves" is well known as an early recognition that physical and chemical properties repeat in intervals of seven elements (the inert gases were not yet known). Other important contributors were the American Josiah Parsons Cooke and British John Herschel ("…Natural Philosophy… and the Rational Chemistry of the Elements" by Ronald Brashear and Gary Patterson), and the German Gustavus Hinrichs (by Gregory Girolami). Cooke with his precise atomic weight measurements has been called among the American chemists of the nineteenth century as "the first university chemist to do truly distinguished work in the field of chemistry." Hinrichs attempted to represent atomic structure three dimensionally; his arrangement of the elements included continuous spirals and showed the importance of long-form Periodic Tables.

But more important to the final appearance and understanding of the Periodic Table were the contributions of the German Lothar Meyer, for whom two full essays are devoted: "The Periodic Table of the Elements and Lothar Meyer" by Gisela Boeck, and "Translation of Lothar Meyer's Modern Theories (1964)" by Vera Mainz. Meyer is not always recognized as a "co-discoverer" of the Periodic Table in the literature, even though his work was simultaneous with Mendeleev's and his periodic organization was essentially the same. As described in Boeck's essay, the main reason Meyer was not recognized was because Mendeleev dared to "predict" elements from the gaps in his Periodic Table. Indeed, the discovery of gallium, scandium, and germanium rapidly followed and Mendeleev was vindicated (although actually, other Mendeleev predictions were not correct and have been ignored in the literature). However, the importance of Meyer's contributions was soon recognized, and dual credit (Davy Medal) was given to both Mendeleev and Meyer by the British Royal Society in 1882. Furthermore, subsequent work of Meyer (1870) clearly showed he more fully understood the implications of periodicity—whereas Mendeleev denied the existence of atoms, Meyer was correlating atomic volume vs. atomic weight, clearly foreseeing that periodicity is reflected not only in the chemistry of the elements but also in the physics. It is amazing that Meyer at such an early year was even considering atomic structure! He was correct that atomic structure was reflected by this periodic behavior, but it was too early to understand why; this had to wait several decades until understanding of electronic structure was formulated.

The question of priority (Mendeleev vs. Meyer) is addressed in the essays of Boeck and Mainz. Meyer's original description of his periodic system had been published in 1864 (5 years before Mendeleev's publication) in his *Die modernen Theorien der Chemie* 1864 in Breslau, Germany (now Wrocław, Poland). The pertinent pages of this have been translated and are provided in Mainz's essay. Meyer's "official" publication, the same where he described a periodicity of atomic volumes dependent upon atomic weight, did not appear until 1870. Hence, priority was not "officially" established by Meyer because he did not publish his "refined" theory first—unfortunately a common story in academia.

Discoveries of the Elements

This section begins with the three elements successfully predicted by Mendeleev—gallium, scandium, and germanium—which were subsequently discovered in minerals in France, Scandinavia, and Germany respectively (essay by Mary Virginia Orna and Marco Fontani). This impressive "prophesy" clinched Mendeleev's fame. Subsequent discoveries, however, gave problems. The rare earths (essay by Simon Cotton) did not fit into the periodicity established by Mendeleev and Meyer, and these elements had to be set aside into a separate row. Next, the inert gases were discovered, but there was not room in the table for them, necessitating the creation of an entirely new column (essay by Jay Labinger). The powerful predictive power of the Periodic Table is underscored by the fact that the Table could rapidly expand like an accordion to accommodate a new family. Ironically, Mendeleev lost the Nobel Prize to Henri Moissan (discoverer of fluorine) because the Periodic Table did not "foresee" the inert gases!

An additional essay ("Birth of the Atomic Age" by Kit Chapman) helps us enter the age of radioactivity and isotopes, discussing how the new elements fit into the Periodic Table. A standing question had been Prout's hypothesis, adopted by some scientists, that the atomic weights of the elements are whole-number multiples of the atomic weight of hydrogen. As molecular weight determinations became more precise, it was clear that Prout's hypothesis did not strictly apply. The discovery of neutrons and isotopes resolved this dilemma.

A final essay in the second section (by Vera Mainz) was a history of Mary Elvira Weeks' life and research, in particular her production of *Discovery of the Elements*. This classical work has served as a framework for many subsequent historical researches. This authoritative treatise passed through several editions, culminating in the expanded 1968 edition with Henry M. Leicester. In this essay Mainz, points out that "Much of the material in *Discovery of the Elements* is as enjoyable and informative today as it was when it was first published in 1932." Indeed, my wife and I used this book as an indispensable Baedeker as we journeyed through our "Rediscovery" travels in 1998-2014, during the new age of GPS, Internet, digital cameras and computers.

The Periodic Table from Other Perspectives

Here the reader is treated with four additional delightful essays. The first, "Astronomy Meets the Periodic Table," by Virginia Trimble, discusses the relationship between astronomical and chemical aspects of the elements. In this essay an interesting discussion is presented of the nuclear generation in stars creating the elements found in our universe. In the second essay of the third section, "Remaining Questions in the 21st Century," Eric Scerri tries to relate outstanding questions to theory, for example understanding subpatterns in the Periodic Table from theoretical considerations, such as the Madelung rule (the sequence of filling up electronic subshells). The third essay, "An Essay on Periodic Tables" by Pekka Pyykkö, continues the discussion of theoretical explanations for "secondary periodicity" and other patterns, and a theoretical look at the Madelung rule. The fourth essay, "A Philatelic Celebration" by Daniel Rabinovich, is a delightful coda to the story of the Periodic Table, where commemorative stamps recognizing important scientists relating to the Periodic Table are described.

Overview

This volume is a remarkable achievement commemorating the IYPT celebration. The strength lies in the completeness of the project. In one book one can dig into the question of "simple substance" vs. element; the subtleties of the triads, and the myriad of other contributors who developed additional models and charts, as well as theoretical and quantum effects, for understanding periodic behavior of the elements. Nowhere have I seen in one source so much rich material devoted to the history of the Periodic Table. I enjoyed studying this book very much, and I happily keep a copy of it now in my book shelf next to Weeks' *Discovery of the Elements* and other historical works. It will serve as both a reference and leisurely reading, and I recommend it heartily for others to enjoy as well.

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1. R. Hoffmann, "Preface," in M. Fontani, M. Costa, M. V. Orna, *The Lost Elements: The Periodic Table's Shadow Side*, Oxford, 2015, p xvi.

Ethics of Chemistry: From Poison Gas to Climate Engineering, Joachim Schummer and Tom Børsen, Eds., World Scientific, 2021, 559 + vii pp, ISBN 978-981-123-353-1, $198 hardcover, $68 softcover, $29.90 ebook.

The 18 papers collected in *Ethics of Chemistry* provide a multifaceted, extensive and thought-provoking set of perspectives on its title subject. It succeeds admirably in what its editors describe as its main purpose, namely to provide an overarching resource on ethics intended for use in university chemistry education—that is, in the education of future chemists. The editors note that the volume could also serve as a cultural history of chemistry in the twentieth and twenty-first centuries. I would phrase it a bit differently while agreeing generally with the claim: most of the chapters can be used as studies of important cases in the history of the intersection of chemistry and society during the last century or so.

The book is inherently interdisciplinary, and many of its chapters involve legal, economic or other social aspects as well as the philosophy and chemistry explicit in the title. The contributing authors are well suited to discuss such interdisciplinary topics: they include chemists, philosophers, educators, and social scientists.

Indeed, many of them, including both editors, can be placed in more than one of these categories. Joachim Schummer has degrees in both philosophy and chemistry. He is founding editor of the open-access online journal *Hyle: International Journal for Philosophy of Chemistry*. Tom Børsen holds degrees in chemistry and chemistry education, and he is director of the Study Board for Techno-Anthropology and Sustainable Design at Aalborg University. Børsen and Schummer were co-editors of special issues of *Hyle* on ethical case studies of chemistry, where the 18 papers collected here were previously published (http://www.hyle.org/journal/issues/special/ethical-cases.html).

The introductory chapter gives a brief introduction to several varieties of philosophical ethics, including consequentialist approaches (in which actions are judged according to their effects) and deontological ones (which focus on *deon*: obligation or duty). In addition, each subsequent chapter includes a sketch of the ethical principles used by the author(s) to analyze the facts described in that chapter's case. Over the course of several chapters, a reader is exposed to a variety of interpretations of ostensibly the same ethical approach or principle.

This pluralism of perspectives is one of the book's strengths. Take for example the precautionary principle, which is invoked in several of the book's cases and explained in some of them. For example, in chapter 8, "When Laypeople are Right and Experts are Wrong: Lessons from Love Canal," Ragnar Fjelland quotes the principle as enunciated in the Rio Declaration from the 1992 Earth Summit:

> Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation.

Fjelland notes that key phrases in the short statement are open to interpretation: how serious are must the potential effects be, and what counts as cost-effective in potential remedies? Lack of certainty, he states, is different from ungrounded fear. Thus, whether or not the principle applies in a given situation is often ambiguous. The principle is interpreted as more broadly applicable in chapter 15, "The Ethical Judgment: Chemical Psychotropics" by Klavs Birkholm:

> Since the human brain, by far the most complex organ in nature, has not yet been satisfactorily mapped by science, it would seem obvious that systematic intervention in its neurochemical processes must inevitably imply a certain, smaller or bigger, risk. … In this situation, the application of the precautionary principle is obviously relevant.

The two chapters mentioned above illustrate the variety of topics addressed in the book. The chapters are arranged, as the editors note in their introduction, in groups according to the kinds of ethical questions raised. The editors note that different orderings would be used if history or chemical discipline were the organizing principle, and add that the chapters can be read or assigned as self-contained articles.

I will attempt to cluster chapters according to ways in which chemistry interacts with the wider society. Adverse effects on the environment, including effects on human health, are the focus of the largest group of chapters. Specific topics in this group include the Bhopal disaster (chapter 5), Love Canal (8), DDT (9), bisphenol-A (10), polyvinyl chloride (11), use of rare earth elements (12), stratospheric ozone depletion (13), climate engineering (14) and chemical regulation (19). Biomedical or biotechnological cases are presented in chapters 6 (thalidomide), 15 (psychotropic drugs), 16 (artificial life) and 17 (DNA and patent law). Military uses of chemistry are discussed in chapters 3 (poison gas in World War I), 4 (napalm), and 7 (agent orange). Professional misconduct is treated in chapters 2 (fabrication or falsification of data) and 18 (codes of professional conduct).

Most of these chapters contain historical content, what might be called case *histories*—making them, perhaps, of greater interest to readers of this journal. Only a few fall outside this category because they are more future-oriented (chapter 14, for example, on climate engineering) or based on fictitious circumstances (chapter 2 on fabrication or falsification of data in research).

In addition to historical content, the book provides a great deal of other practical information that is not typically included in undergraduate chemistry education—information very relevant for chemists who work outside academic research. The relationships between suppliers of chemical commodities and manufacturers of consumer products and the different considerations they may face over the same material were brought out particularly in three chapters in the middle of the book. Abigail Martin and Alastair Iles examine ethical aspects of bisphenol-A, polyvinyl chloride and rare earth elements (with Christine Rosen on the first two). Each of these chemicals is produced by one set of companies and used by other companies in products sold to end users. Both sets of companies have an obligation to consider the possible environmental harm involved in production

(for example, in mining and refining rare earth elements) as well as the possible harm to end users (such as possible endocrine-disrupting effects of bisphenol-A in the lining of food containers or bottles) and the fate of the chemical at the end of the product's life. Some of these issues are more immediate for the initial extractors and producers, others for later users; however, companies at different points in the chain are stakeholders that can influence their suppliers, individually or collectively, just as end-users or consumers can influence their suppliers.

Broadening one's perspective from the chemical details of immediate concern is a theme that permeates the book, and it is a theme that applies to academic chemists as well as those who work for industry. That chemists have a duty to consider foreseeable consequences of their work is asserted in many chapters. Consequentialist approaches to ethics do not excuse unintended effects, and deontological approaches include a duty to avoid doing harm, a duty that requires reasonable foresight.

I was struck by several examples of consequences that I had not previously considered. For example, Schummer writes, "any new highly toxic substance that might be researched for some pharmaceutical effect is at the same time, by its toxicity, a new potential chemical weapon." The next sentence, "Thus, if you first synthesized it, you are co-responsible for its possible military or terrorist abuse by anyone in the future," seems to me too restrictive—a blanket condemnation of such activity. I agree, though, that that risk ought to be considered and weighed against the likely benefits of such a substance. Along the similar lines, Claus Jacobs and Adam Walters raise the issue of "publishing as proliferation" in their chapter on Agent Orange. They suggest that publishers of even basic research share responsibility for the risks associated with a new agent whose synthesis they publish. Jeffrey Kovac, in his review of codes of ethics promulgated by the American Chemical Society (ACS), notes that the ACS "Ethical Guidelines to Publication of Chemical Research" gives both authors and reviewers the responsibility to inform the editor about concerns that a manuscript provides knowledge that could be reasonably expected to be harmful.

One other very broadly applicable idea that struck me was a duty of chemists to use their expertise to research and warn against possible harms to society. Schummer's chapter on stratospheric ozone depletion describes the work of Mario Molina and Sherwood Rowland on this subject as the example par excellence of such research. Schummer derives a duty of scientists to warn against harm from a more generally applicable duty to rescue (a person from drowning, for example).

I hope that I have made it clear that I have not been persuaded by all of the authors' ethical judgments. I count the book as successful for the questions it raises—and I suspect that the authors would be pleased with such a criterion.

As a final note, I would like to echo the editors' hope that this book finds use in the university education of chemists. Ethical conduct or ethical awareness are mentioned in the educational guidelines for approved university programs in chemistry published by both the ACS and the United Kingdom's Royal Society of Chemistry. My own experience in the US system of higher education leads me to believe that courses devoted to ethics of chemistry are not common. Perhaps more common are "capstone" courses in which students are asked to integrate aspects of earlier chemistry courses. Whether or not such courses have ethics as a focus, case studies from *Ethics in Chemistry* would be suitable for such courses—and they would bring ethical questions to the classroom.

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The History of the Woodward Hoffmann Rules, Jeffrey I. Seeman, *The Chemical Record*, 2021-. [The subject of this review is series of historical articles currently being published in monthly installments within a periodical. Such serial publication was once common for novels, but is unusual in history of science. Whether one considers the result to *be* a book or to be *like* a book, we present a review of the first seven installments (of 27), published in the January-May 2022 issues. —the Editor]

Jeffrey Seeman is in the process of publishing a history of the development of the Woodward-Hoffmann Rules (Conservation of Orbital Symmetry) to include a total of twenty-seven articles. To date, seven papers have appeared in *The Chemical Record*. The size and scope of this endeavor can only be hinted at by referring to the cumulative journal page count (284) of these first seven papers, which include numerous photographs, many quite rare, and hundreds of references and are, in part, based upon numerous interviews. Among these are valuable commentaries from Roald Hoffmann, typically incisive and balanced, throughout these articles. Each article begins with a list of the titles of all twenty-seven papers, providing a road map of the entire journey. Despite this seemingly imposing demand upon the reader, the articles are very engagingly written, nicely cross-referenced, highly illustrated and, quite frankly, a joy to read. Indeed, the first paper is wonderfully illustrated with colored caricatures, by artist Chip Cooper, of many of the scientists cited in the series. These caricatures alone are "almost worth the price of admission." Since the articles appear separately in journal format, Seeman frequently repeats material in order to bring readers "up to speed," refresh memories and renew context. This is a strength for the series and one that, if eventually assembled into a book, suggests some pruning could be helpful. One must note perforce that the present review must skip very lightly over the enormous wealth of information provided in only these first seven papers. One slight criticism is that the papers have a surprising number of small errors in omission of words and typos. These do not significantly impact the superb quality of the articles, although in the heading of Paper 4 (Part 1) Fukui's year of death is printed as 1981 (the year he shared the Nobel Prize with Road Hoffmann) instead of 1998.

The first article is an overview of the series and establishes the multiple approaches by Seeman in his very "deep dive" into the background of experiment and evolution of theory. He characterizes his overall methodology to include: a) classical review of the relevant chemistry, b) classical history of the relevant chemistry, c) sociology of science, d) social construction of science, and e) psychology or dynamics of motivation—this last one fascinating for its analyses of excesses on a continuum of strengths and weaknesses. The author reintroduces the term "sleeping beauties" to describe important theoretical and experimental discoveries published but barely noticed by the experimental and theoretical chemistry communities. Particularly noteworthy were the publications of Luitzen Oosterhoff (theoretician), Egbert Havinga (experimentalist) and his graduate student Jos Schlatmann at the University of Leiden, and Kenichi Fukui (primarily from a theoretician's viewpoint) at Kyoto University. Mentioning early the accusation by Elias J. Corey, in 2004, of plagiarism (to be discussed in considerable detail in later papers in this series), Seeman introduces readers to the "Rashomon effect" popularized by the famous 1950 Kurosawa film in which different observers offer unique interpretations of the same incident. Lesser known is the "Merton effect," referring to the rarity of "singleton" discoveries in science, as opposed to nearly simultaneous multiple related discoveries. An example that has long impressed this reviewer was the publication of tetrahedral carbon, virtually simultaneously and independently by van't Hoff and Le Bel in 1874, both working at the time with Wurtz.

Early experimental curiosities, awaiting rationalization based upon theory, were thermal isomerizations of substituted cyclobutenes to 1,3-butadienes, noted by Emanuel Vogel (1954) and Rudolph Criegee (1959), in which the less thermodynamically-stable product was formed. Most cited were the observations by Havinga and Schlatmann, in their studies of vitamin D published in 1961, of the alternation of thermal and photochemical stereochemistries and the accompanying alternation of 4π- and 6π-conjugated electron systems. In 1963, Corey and Alfred Hortman observed similar alternating thermal and photochemical valence isomerizations as did Robert Burns Woodward and Subramania Ranganathan during 1963-64. Seeman also refers back to a paper by A. Wasserman in 1935 in which two reactants "choose" Diels-Alder ("4 + 2") reaction over the competing "2 + 2" reaction despite both being significantly thermodynamically favored, albeit the Diels-Alder more so. Aside from advising a generation of outstanding researchers who contributed to this field, William von Eggers Doering explored what he termed "no mechanism" reactions (1962), characterized by the lack of intermediates and weak sensitivity to solvent effects. In 1952 Doering recognized the "2 + 4n" rule, consistent with aromaticity, although n = 0 was not specifically recognized until

Ronald Breslow reported the triphenylcyclopropenium ion in 1957. Anti-aromaticity was not explicitly recognized until the 1960s. The explicit connection between aromaticity, anti-aromaticity and the theory provided in 1931 by Erich Hückel had a singular triumphant "moment" in the 1960s with Franz Sondheimer's synthesis of [18]-annulene (*i.e.*, n = 4). Following Woodward and Hoffman's 1965 ground-breaking papers disclosing the ramifications of the conservation of orbital symmetry, Michael Dewar and Howard Zimmerman proposed complementary explanations based upon aromatic and anti-aromatic transition states (including potential Möbius variants).

Seeman reminds readers that until the 1960s, the symmetry characteristics (*e.g.*, phases) of orbitals were not explicitly considered by most organic chemists and textbooks in presentations of stabilizing conjugative interactions. While Dewar's model of a complex between silver ion and ethylene, in the early 1950s, explicitly displayed stabilization resulting from in-phase overlap of a d-orbital on silver ion and a π*-orbital on ethylene, for example, textbooks by John D. Roberts (1961) and Andrew Streitwieser (1961) communicated the necessity for widespread understanding of ground-state stabilities. However, in papers co-authored with Haruo Shingo in 1952 and 1954, Kenichi Fukui had applied, what he termed, frontier molecular orbital theory to demonstrate that the p-orbital coefficients of the highest occupied molecular orbital rationalized regiospecificity in the electrophilic substitution reactions of naphthalene and related aromatics, as well as nucleophilic attack on the lowest unoccupied molecular orbital. In 1964, Fukui published a book chapter in which he employed the symmetries of frontier molecular orbitals of diene and dienophile to explain the concerted Diels-Alder reaction. This was certainly a major contribution toward his shared Nobel Prize. As Seeman notes, had Woodward not died in 1979, he surely would have shared the 1981 Nobel Prize with Hoffmann and Fukui.

Paper 4 is comprised of Parts I, II, and III and provides a very extensive and rare presentation of the life and science of Kenichi Fukui. Admittedly, this reviewer knew little about the pursuit of chemistry research in Japan, and the obstacles encountered, in the decades immediately following World War II. The thoroughness of Seeman's coverage includes rare photographs and communications with, among many others, Tetsuya Fukui, son of the Nobel laureate, and Gernot Frenking, who was a post-doctoral associate of Professor Fukui between 1973 and 1975. In contrast to the many young Japanese scientists who came to study and engage in research in the United States and other Western nations during the 1950s and 1960s, Fukui had no such opportunity. His genius, dedication, discipline, independence and rigor were the key elements of his early discoveries and rise through the ranks in Kyoto University. Seeman's "leisurely guided tour" through the three dedicated Fukui papers provides considerable insight into the university system and chemistry enterprise in Japan post World War II. In 1940, Fukui was a third-year student at Kyoto starting experimental research. His most influential chemical mentors Gen-itsu Kita and Shinjiro Kodama helped spare him from the draft and connected him with research opportunities. Fukui performed experimental research in the Japanese Army Fuels Laboratory (1941-43), joining Professor Kodama's *koza* as a Lecturer in 1943, then Associate Professor in 1945 and completing his doctorate in 1948. Professor Fukui's research career encompassed an astoundingly wide array starting with chemical engineering, experimental organic and polymer chemistry, and the theoretical chemistry that would merit the Nobel Prize. At one point early in his career, he directed two *kozas*- one experimental and one theoretical. He also produced over one hundred patents.

The final paper reviewed here (Paper 5; *i.e.*, the seventh journal article) is titled "The Many Chemists Who Could Have Proposed the Woodward-Hoffmann Rules (Including Roald Hoffmann) But Didn't: The Theoretical and Physical Chemists" and returns to the early insights of Oosterhoff and Fukui and then describes in great detail the relevant research of nineteen other scientists, most very well known names, but interestingly describing two papers (1955 and 1957) published by Virginia Griffing, professor of physics at Catholic University. The next article (Paper 6), promised to readers in the near future, treats organic chemists who similarly missed their full opportunity.

Jeffrey I. Seeman and this reviewer are true contemporaries (born 1946; B.S. 1967; Ph.D. 1971). For this reviewer, description of the merger of mechanistic organic chemistry with theory at the level of Hückel theory during the 1950s and early 1960s fills many gaps in historical context. While important textbooks such as Edwin Gould's *Mechanism and Structure in Organic Chemistry* taught well the role of π-conjugation, including quantitative linear free energy relationships, the role of orbital symmetry (phase) and frontier molecular orbitals awaited the next decade's textbooks. Still, starting in the latter half of the 1960s qualitative molecular orbital theory quickly became part of our own paradigm

as if these models had already been in common use for decades. Thanks to Fukui, Hoffmann, Woodward and scores of distinguished scientists we were gifted with an armamentarium with which to understand aromaticity, anti-aromaticity and the relative activation energies and stereochemistries of a vast array of chemical reactions, thermal and photochemical, concerted and non-concerted. Following an accomplished industrial career, Seeman has already made his mark in the history of chemistry developing the 20-volume series titled *Profiles, Pathways and Dreams* (ACS; Oxford University Press), each an autobiography of a famous chemist, and initiating and administering the *Citation for Chemical Breakthrough* Award, recognizing seminal papers, books and patents. However, this new series, hopefully edited into a book, may become his most lasting legacy. One may compare and contrast Seeman's exploration of the development of the conservation of orbital symmetry with studies of the history of the periodic table. That story is, of course, far more complex than "simply Mendeleev." However, the ability to interview major actors and their collaborators aided by telephone, airmail, email, remote conferencing, digitized archives, and the airplane allow for far greater depth, currency and diversity of viewpoints than could be brought to bear in studying the history of the periodic table. All of these have been diligently exploited by Seeman and we are the fortunate recipients of this treasure trove.

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RSC Historical Group Talks on Video

Recordings of the talks given to the Royal Society of Chemistry Historical Group are now grouped together in a single playlist in the RSC YouTube Channel at https://www.youtube.com/playlist?list=PLLnAFJxOjzZu7N0f5-nVtHcLNxU2tKmpC

The talks have been given since July 2020, although they were only recorded regularly since the start of 2022. The series started life as lockdown webinars but they are still continuing. Currently there are two series, the main series which takes place each third Tuesday of the month (except August) and a series covering the history of chemistry between 2019 and 3000 BCE, loosely based on the recently published Bloomsbury *Cultural History of Chemistry*, which is on the fourth Tuesday of each month (except August and December).

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Articles of 4-20 pages, double-spaced (excluding references) should be submitted electronically by email attachment to the Editor, giunta@lemoyne.edu, at Le Moyne College. The title of the article should be of reasonable length (up to 15 words); a subtitle may be included if appropriate. Authors should strive to make the title descriptive of the specific scope and content of the paper. Preferred file formats for submissions are .doc, .docx, and .rtf.

Subheadings within the paper are often appropriate to enhance clarity. Authors should bear in mind, however, that the format of an article in history of chemistry (order and content of sections) is not the same as the format of an article in chemistry. Recent issues of the *Bulletin* should serve as a guide. Detailed text formatting (paragraph justification, for example) need not be imitated, however; such text formatting will be applied at the layout stage. The *ACS Guide to Scholarly Communiction* (Banik, Beysinger, Kamat, and Pienta, 2020, https://doi.org/10.1021/acsguide) is a useful resource for names, terms, and abbreviations appropriate for writing about chemistry—but not for references. (See below.)

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Please provide a short biographical paragraph, to be included as **About the Author(s)** at the end of the article.

The Back Story

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Dudley Herschbach, a Doorway to a New World

Dudley Herschbach has always been "all in." In high school football, he played both varsity offense and defense. He made his life decision when faced with Stanford University's offer of both an athletic and academic scholarship. He chose academics. But throughout his life, Dudley has always chosen fun, too.

Dudley's reputation is based on his studies of the dynamics of chemical reactions in crossed molecular beams. Dudley shared the 1986 Nobel Prize in Chemistry with Yuan T. Lee and John C. Polanyi "for their contributions concerning the dynamics of chemical elementary processes." Creating something new—for Dudley, this was a new field of research—is what science and scientists are all about. What Dudley also does is opens doors, big doors, for others.

"I was making nylon at my lecture at Cornell College, a small liberal college in Mount Vernon, Iowa, in 1988. Many students were bused, some coming from considerable distance, two hours! It was a Saturday, and the audience was very large, several hundred. At my freshman course at Harvard, I did jump up on the table with nylon. I did a lot of demonstrations but not often jumping up on the table" (2).

In addition, Dudley's list of over 500 publications is what might be expected: 136 in the *Journal of Chemical Physics*, 62 in the *Journal of Physical Chemistry*, 21 in *Chemical Physics Letters*, and so on. But scattered throughout the list, and especially in the last several decades, is an ever-increasing number of papers dealing with the history of chemistry. And many are memorials to his friends and colleagues, a burden that comes when one is blessed with long life.

Here I focus on just one of Dudley's publications to illustrate the knowledge-density in Dudley's offerings, which he provided in a most user-friendly fashion. This is an example of opening doors to the reader. Dudley has been an admirer of Benjamin Franklin for years. *Ben Franklin's Scientific Amusements* (1) is a record of a lecture he presented to the Academy of Arts and Sciences in January 1995. Dudley presents us with a mini-biography of Franklin. And Dudley is a skillful entertainer. What better way to educate than while entertaining! Dudley's magic is so persuasive. He began and closed his lecture with music. So we shall follow Dudley's orchestration.

Please consider listening to Benjamin Franklin's *Quartetto for Three Violins and Cello*, https://www.youtube.com/watch?v=XR4mlR3laik which, as related by Dudley (1) employs three violins and a cello, with scordatura tuning such that each musician has to play only four notes, one on each of the open strings. The result is sixteen-tone music, vastly simplified for the performers! I still remember that the string players had quizzical expressions on their faces; their left hands were used to fingering like mad but in this quartet had nothing to do. Certainly the piece, whether or not composed by Franklin, exhibited his yen for whimsical, pragmatic invention.

Dudley then takes the audience through many of Franklin's scientific amusements: ocean currents; color and heat absorption; earthquakes, the aurora borealis, his invention of the "Pennsylvania Stove;" comets; eclipses of the moon; motion of storms; perspiration and the bloodstream; electricity and lightning rods; population estimates; evaporation; spreading of oil on water; mapping the Gulf Stream; bifocal eyeglasses; rigging for swift vessels; design of a sea anchor. I did not know that "the lightning strike really goes up, not down" (1). Dudley summarizes, "Much that he did was for the sheer fun of it" (1). This speaks for Dudley as well.

Both Dudley's article on Franklin and this Back Story end with a glass armonica concert. Yes, Franklin invented that musical instrument too. Please join in the fun: https://www.youtube.com/watch?v=g_kPOI5wPZE .

Thank you Dudley, and good evening to you and Georgene.

1. D. Herschbach, "Ben Franklin's Scientific Amusements," *Bull. Am. Acad. Arts Sci.,* **1994**, *48 (October)*, 23-43.
2. D. Herschbach, email to J. I. Seeman, Sept. 18, 2020.

The BULLETIN FOR THE HISTORY OF CHEMISTRY (ISSN 1053-4385) is published biannually by the History of Chemistry Division of the American Chemical Society. All matters relating to manuscripts, book reviews, and letters should be sent to Dr. Carmen J. Giunta, Editor. Subscription changes, changes of address, and claims for missing issues, as well as new memberships, are handled by the Sec./Treas.

BULLETIN FOR THE HISTORY OF CHEMISTRY
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Manlius, NY 13104

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